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The Influence of Selected Metal Traces
on the Color and Color Stability
of Purified Cotton Linters

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THE INFLUENCE OF SELECTED METAL TRACES ON THE COLOR AND COLOR STABILITY OF PURIFIED COTTON LINTERS

A thesis submitted by

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GLOSSARY

Brightness. The reflectance, measured under standardized conditions, of a sheet of pulp or paper toward blue light having an average wavelength of 457 mmu.

Brightness reversion. The reduction in brightness which pulp or paper undergoes as a result of natural or accelerated aging.

Specific absorption coefficient. That fraction of incident light which is absorbed by a thin layer of material divided by the basis weight of the layer. It is expressed in reciprocal basis weight units, e.g., sq. cm./g.

Specific scattering coefficient. That fraction of incident light which is scattered backwards by a thin layer of material divided by the basis weight of the layer. It also is expressed in reciprocal basis weight units.

INTRODUCTION

The property of brightness and the phenomenon of brightness reversion have become increasingly important to the paper industry because of consumer demand for products of high brightness. Although technical methods for attaining high brightness levels in pulp and paper are fairly well developed, the means of effectively preventing reversion are not known. Moreover, the future development of rational techniques for eliminating reversion is precluded by a lack of knowledge regarding the causes, mechanisms, and rate-controlling factors in this phenomenon.[1]

Although there is little direct experimental evidence that sorbed metal salts may induce brightness reversion, occasional publications (1, 3-8) have appeared which suggest such a possibility. In addition many other investigations clearly indicate that metal salts affect the rates and products of several cellulose reactions. For example, metal salts impair the permanence of paper (9, 10), they accelerate the oxidation of wood pulps (11-14) and cotton cellulose (15, 16) with hypochlorites and peroxides (14, 17), and they accelerate autoxidation of alkali cellulose (18). If the reactions involved in reversion are at all similar to these reactions, then metal salts might be expected to affect brightness reversion as well.

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[1]The literature on brightness reversion was reviewed by Rollinson (1); opinions expressed on this subject during an international symposium on bleaching were summarized by Talwar and McDonnell (2).

PRESENTATION OF THE PROBLEM

A review of the literature on brightness reversion and the reactions of cellulose suggests that salts of metals may be detrimental to high brightness in paper, either by directly imparting color or by accelerating reversion.

The purpose of this investigation was to observe and interpret the effects of small amounts of selected metal salts upon the brightness and brightness stability of handsheets made from a highly purified cotton linters pulp. Specific objectives were:

1. to observe whether or not the addition of small amounts of ferric, ferrous, cupric, and manganous salts affect the color and color stability of handsheets;

2. to determine whether or not variables, such as moisture content and temperature, in accelerated aging, affect metal-induced reversion; and

3. to infer, if possible, the nature of the reactions which occur during metal-induced reversion.

ANALYSIS OF THE PROBLEM

When paper undergoes a loss of brightness as the result of either natural or accelerated aging, materials must be formed or rearranged within the pulp fibers so as to absorb light in the visible region of the spectrum. Although the possibility exists that reversion is strictly a physical phenomenon due, for example, to the migration of colored bodies from fiber interiors to fiber surfaces, there is little evidence to support this hypothesis. Moreover, the results of recent reversion studies point to chemical changes as the more likely cause of reversion as it is commonly encountered. Consequently, primary consideration should be given to the chemical changes required for color formation from cotton linters.

Specifically, metal salts could bring about losses of brightness in cotton linters pulp in the following ways:

1. By forming inorganic colored materials via:

    a. complex formation with cellulose or its degradation products;

    b. salt formation with the degradation products of cellulose;

    c. hydrolysis of metal salts;

    d. oxidation of metal salts; and

    e. reactions between metal salts and the residual, minor constituents of the plant fiber.

2. By promoting the formation of organic colored materials via:

   a. photolytic degradation of cellulose;

   b. pyrolytic degradation of cellulose;

   c. oxidative degradation of cellulose;

   d. hydrolytic degradation of cellulose;

   e. reactions of minor constituents of the linters; and

   f. reactions of the degradation products of cellulose.

The experimental program should distinguish between reversion occurring as a result of organic and inorganic reactions. Reversion arising from inorganic reactions should be recognizable by observing the extent to which brightness returns to its original level when the added metal salts are removed with dilute acid. Any reversion brought about by irreversible organic reactions would probably not be affected by such an extraction.

Inasmuch as metals do not tend to form highly colored salts or complexes with cellulose or simple carbohydrates, it seems unlikely that materials of this type would contribute much color to handsheets made from cotton linters. Development of color via complex formation with degradation products could conceivably occur, but without knowledge of the structure of these degradation products the importance of such complexes in reversion cannot be predicted.

Many metals salts, e.g., ferric sulfate, react readily with water to form slightly soluble hydroxides that are more deeply colored than the original salt. Since water will be present on the cellulose during

aging, this phenomenon may be important. Moreover, hydrolysis of the salts liberates acid which could react with the linters to produce color. If hydrolysis of salts is a cause of reversion, then correlation of the basic strengths of the metals with their reversion-accelerating ability would provide an indication of this possibility.

Oxidation of metal salts to more highly colored compounds, e.g., ferrous to ferric salts, should also be considered. This type of reaction would require that an oxidizing agent be present and that the initial oxidation states of the metals permit further oxidation. The addition of the highest stable oxidation state of a metal would exclude this reaction, and the addition of lower states of oxidation would require the participation of atmospheric oxygen or other oxidant to develop the color associated with the higher state of oxidation. Some measure of the importance of this type of color formation therefore, might be gained by comparing the results of aging in air and in nitrogen.

Since cotton linters contain small amounts of other substances besides cellulose, organic or inorganic reactions involving minor constituents might play an important role in reversion. In order to minimize the contribution of minor constituents to reversion, as pure a grade of cotton linters as is available should be selected.

Cellulose undergoes discoloration and physical degradation on exposure to light, particularly ultraviolet radiation. If, however, aging is conducted in light-tight chambers, the contribution of photolysis to reversion may be regarded as negligible.

When heated in an open system, cellulose fibers lose water. At low temperature and short exposure times only condensed water is removed. As the temperature and exposure time increase, however, water of constitution may also be removed and pyrolysis occur. Because there is no sharp transition between drying and pyrolysis, the temperature and duration of accelerated aging should be so chosen as to reduce pyrolysis to a minimum.

In the presence of oxygen at elevated temperatures cellulose undergoes oxidation to form a variety of products, some of which are unsaturated. Even cellulose that has been treated with an excess of powerful oxidants, however, does not usually appear colored. Pulps having high carbonyl contents as a result of oxidation during bleaching are generally observed to undergo reversion to a greater degree than pulps with low carbonyl contents (19, 20). This would imply that reversion may be the result of additional reactions following oxidation. If air oxidation is contributing to reversion, this fact could be determined by aging in the absence of oxygen and comparing the results with those obtained for aging in air.

Cellulose is sensitive to acid hydrolysis because of its β-1,4 glucoside structure. Limited, random hydrolysis of cellulose would be expected to reduce D.P. and to increase the number of reducing end groups. Accordingly, the reversion process could be followed by viscosity measurements to provide one indication of the occurrence of hydrolytic chain scission.

Hydrolysis alone cannot produce colored materials from cellulose. But, if hydrolysis is extensive or localized enough, low molecular weight carbohydrates would be formed which, upon undergoing appropriate additional reactions, could lead to color formation. Of the various pathways by which colored substances are formed from carbohydrates the most plausible might well be via the furans. Moreover, since glucose is virtually the only simple sugar resulting from the hydrolysis of purified linters, the detection of hydroxymethylfurfural (HMF) would indicate that at least some of the products causing reversion could be formed via the furan pathway.

EXPERIMENTAL MATERIALS AND METHODS

CELLULOSE

An acetate-grade of cotton linters pulp was used throughout this investigation. This pulp was obtained from the Buckeye Cellulose Corporation and was labelled:

"Cotton Linter Pulp, Type 1-AR-2000, Sr. No. 904."

Results of analyses characterizing the linters are shown in Table I.

Immediately prior to use, portions of the pulp were slushed at 1.6% consistency and soaked in a mixture of hydrochloric (0.1N) and hydrofluoric (0.1N) acids for about 15 hours. After being filtered and thoroughly washed with 1 liter of deionized water for every 5 grams of linters to remove all traces of acid, the pulp was used to make handsheets. The effectiveness of this treatment in reducing the iron and ash content of the pulp may be seen in Table I.

Preliminary tests (Trial I) showed that acid washing had very little effect on the initial absorption coefficient, k_o, or absorption coefficient after accelerated aging (see Table I).

TABLE I

PROPERTIES OF COTTON LINTERS PULP

	Untreated Pulp		Acid Washed Pulp
	a	b	c
Alpha-cellulose, %	99.6	—	—
Beta-cellulose, %	0.1	—	—
Gamma-cellulose, %	0.3	—	—
Soda solubles, %	0.7	—	—
Ash, %	0.040	0.041	0.003
Calcium, p.p.m.	27	—	—
Iron, p.p.m.	10	16	4
Manganese, p.p.m.	<0.1	0	0
Copper, p.p.m.	—	0	0
Viscosity (A.C.S. cupram), sec.	1700	—	—
Intrinsic viscosity (TAPPI cuprien.), dl./g.	—	15.2	13.6
D.P.[d]	2240	2280	2040
Absorption coefficient, sq.cm./g.[e]			
unaged	—	1.45	1.21
aged 2 hours	—	1.72	1.58
7 hours	—	2.06	1.94
18 hours	—	2.55	2.68
42 hours	—	3.57	3.57

[a] [b, c] Determined by Buckeye Cellulose Corporation
Determined by author
[d] Estimated from monographs and equations of Gloor and Klug (31)
[e] Measured in Trial I; aged at about 103°C. and about 5% moisture.

WATER

Deionized water was prepared by passing distilled water through an ion-exchange column charged with Amberlite MB-3 resin. The pH of this water was close to 7.0 immediately after passage through the column, and was in the range of 5.5 - 6.0 after standing in the air for several minutes. Iron, copper, and manganese could not be detected in the treated water by chemical analysis. The specific conductance of this water was 0.3×10^{-6} ohm^{-1} cm^{-1}.

METAL SALT SOLUTIONS

Small amounts of iron, copper, and manganese are frequently found in process waters as a result of corrosion, insufficient purification, and other causes. Moreover, these metals are readily sorbed by cellulose fibers and may have noticeable effects on reactions involving cellulose. Iron, copper, and manganese therefore were selected for intensive study; other metals, e.g., aluminum, cadmium, lanthanum, and magnesium, were used in single experiments.

With the exception of two trials, sulfate salts of the metals were used. Analytical or reagent-grade salts were dissolved in deionized water, and aliquots of these solutions added to the pulp slurries as desired. The concentrations and pH of the various salt solutions are given in Table II.

The hydrogen-ion concentration of the iron salt solutions was adjusted to pH 2.2 with concentrated sulfuric acid to prevent the

formation of colloidal hydroxides which would have been filtered out during sheet formation. Although the hydrogen-ion concentration of the salt solutions varied as a result of either hydrolysis or adjustment, such small amounts of them were added to the pulp slurries that the pH of the slurries remained essentially unchanged, i.e., about 4.5 - 5.5 after the addition of salt solutions.

TABLE II

METAL SALT SOLUTIONS

Salt	Concentration,		pH	
	g. metal/l.	moles metal/l.	unadjusted	adjusted
Ferric sulfate	0.100	0.00179	3.0	2.2
Aluminum sulfate	0.100	0.00372	3.9	—
Ferrous sulfate	0.100	0.00179	4.8	2.2
Cupric sulfate	0.100	0.00157	5.0	—
Manganous sulfate	0.100	0.00182	5.5	—
Cadmium sulfate	0.202	0.00180	5.3	—
Lanthanum sulfate	0.250	0.00180	—	—
Magnesium sulfate	0.0437	0.00180	8.6	—

ADDITION OF METAL SALTS AND SHEET FORMATION

In order to have control over the species and amount of metal present in cellulose, the effects of metals were observed by deliberately adding small amounts of metal salts to pulp slurries, and measuring, both before and after aging, the specific absorption coefficient of handsheets made from the slurries. A control containing no added metals was also included in every experiment.

The equivalent of 8 grams of ovendry, acid-washed pulp was suspended in 2 liters of water and dispersed for 15,000 revolutions in a TAPPI standard disintegrator. This slurry was immediately divided into two equal portions each of which was diluted to 2 liters. To each portion the equivalent of 2 mg. of a metal was added from one of the metal salt solutions. Each slurry then contained 1 microgram of metal per milliliter of water or 0.5 mg. metal per gram of pulp. The metal-containing slurries were divided into equal portions and filtered on a Buchner funnel to form four handsheets (reflectance pads).

The preparation of the reflectance pads was in accordance with Institute Method 412-2 with the following exceptions: The pulp slurry comprising 2 grams of ovendry fiber and 1 liter of water was filtered on <u>two</u> sheets of 15-cm. filter paper instead of one to prevent the holes in the Buchner from marking the pad. Furthermore, after the pad had been formed and blown on the single sheet of 18.5-cm. filter paper, the two sheets of 15-cm. paper were carefully removed from the wet pad and replaced by a new standard blotter. This procedure was necessary

to avoid the highly undesirable fuzzing of the pad that occurred when the 15-cm. filters were removed after pressing or drying.

When the pads were being placed into drying rings, the blotter used to replace the 15-cm. filter papers was removed and replaced by a single sheet of 15-cm. filter paper to protect the pad during drying.

After being dried, disks were cut with a 9.0-cm. (diam.) die from the center of each 2-g. pad. These disks were accurately weighed under the same constant humidity conditions in which they had been dried so that their basis weights, W, in g. per sq. cm. could be calculated. The disks were then ready for initial optical tests or conditioning prior to aging.

A minimum of four reflectance disks were made for each sample, e.g., the control or pulp treated with a metal salt, to be tested. Two of these disks were used for the determination of the absorption coefficient and the other two were used as backing and protective padding for the two disks actually used in the reflectance measurements.

DETERMINATION OF THE SPECIFIC ABSORPTION COEFFICIENT

For the measurement of reversion it is desirable to use an optical property of handsheets that can be related directly and easily to the amount of color formed during aging. Although the brightness of paper is normally evaluated in terms of reflectance, reflectance per se is of little fundamental value because it is not linearly related to chromophore concentration. For example, it may be demonstrated

that a 10-point loss of brightness from 80 to 70% G.E. requires a far greater increase in chromophore concentration than an identical loss from 90 to 80% G.E.

A more satisfactory optical property of paper is the Kubelka-Munk specific absorption coefficient, k, (21, 22) which has been shown to vary linearly with the concentration of dyestuff added to paper (23). If color reversion is regarded as the formation of dyestuffs in pulp, then values of k should provide a reliable means of determining how much of these materials are formed during aging.

Values of k for cotton linters pulp were determined from measurements of the reflectance, R_o, of a single reflectance disk backed by a black body, and the reflectance, R_∞, of the disk backed by several layers of the same material. These measurements were made on the General Electric Recording Spectrophotometer (GERS) in reference to a magnesium carbonate block.

Two of the four reflectance disks prepared for each sample were used in the measurement of k. The R_o of each disk was measured at 457 mmu for ten different points on the disk and the readings averaged. The R_∞ of the same disk was next measured at 457 mmu for five different points and these readings averaged. The average reflectances (R_o and R_∞) were used to determine the value of the product, kW, (where W is the basis weight in grams per square centimeter) from the Kubelka-Munk Charts (24) relating R_o and R_∞ to kW. The basis weight, W, of the disk was then divided into kW to yield the value of k in square

centimeters per gram. Values of k for each disk were averaged to give k for the sample.

An analysis of variance for scattering coefficients, s, in Trials II-IV (see EXPERIMENTAL RESULTS p. 24-5) suggested that an alternative method for determining k could be used without significantly impairing the accuracy of the results. In this alternative method the average reflectances (R_o and R_∞) for disks from ten samples in a trial were used to determine values of sW from the K-M chart. The basis weights, W, of the disks were divided into sW to yield values of s in square centimeters per gram. The average value of s for the ten samples was then used to determine k by multiplying s into the ratio k/s which had been calculated for each sample from the average R_∞ according to the equation, $k/s = (1-R_\infty)^2/2R_\infty$ (21). This alternative method was much less time consuming than the first method and was used in Trials V - XIII.

When it was desirable to record either reflectances or absorption coefficients as functions of wavelength, the following procedure was used: on a reflectance disk representing the desired sample, a point, having a value of R_o at 457 mmu corresponding to the average R_o for the disk, was selected and a curve of R_o vs. wavelength recorded for this average point. Similarly a point corresponding to the average R_∞ of the disk was selected and the reflectance curve determined. Values of k at wavelengths other than 457 mmu were then determined using reflectance data read from these curves.

All average reflectances ($\underline{R}_o$ and $\underline{R}_\infty$) were corrected to the absolute scale of reflectance prior to their use in the determination of $\underline{k}$. The corrections necessary are discussed in the APPENDIX p. 103.

CONDITIONING PRIOR TO AGING

After their initial absorption coefficients had been measured, the reflectance disks were conditioned in atmospheres of known relative humidity in order to control their moisture contents at various desired levels. Atmospheres of known relative humidity were maintained in desiccators with saturated salt solutions. The salts used, the relative humidity above their saturated solutions (25), and the moisture contents of cotton linters pulp after 24 hours exposure to this relative humidity are given in Table III.

After being conditioned in one of these atmospheres for about 24 hours, the samples were quickly sealed in aging chambers and aged.

ACCELERATED AGING

Accelerated aging has commonly been conducted in circulating atmospheres at temperatures close to 100°C. and relative humidities approaching 0%. Although aging under these conditions is convenient, it has the definite disadvantage that fiber desiccation occurs to a degree seldom encountered elsewhere.

In order to overcome this objection, accelerated aging was conducted in sealed chambers having low internal volumes. The purpose

of sealed chambers was to maintain a nearly constant moisture content in the pulp during aging at elevated temperatures. If a sufficient fraction of the internal volume of a sealed chamber is filled at room temperature with pulp containing moisture, then during accelerated aging at approximately 100°C. the moisture content of the pulp does not change greatly because the liquid water on the pulp has little free space into which it can vaporize. Calculations based on a materials balance indicate that for the particular chambers used in this research, 97% or more of the initial moisture is retained if 10 or more grams of pulp containing 5.5% moisture are present in the chamber during aging. These calculations are included in the APPENDIX, p. 104.

TABLE III

CONDITIONING ATMOSPHERES AND MOISTURE CONTENTS OF COTTON LINTERS PULP

Salt	Relative Humidity, %[a]	Moisture Content of Pulp, %
Potassium chromate	86.5	11.2-11.4 [c]
Sodium chloride	76.5	9.4-10.1 [c]
-- [b]	50	6.7- 7.1 [d]
-- [b]	50	5.1- 5.3 [c]
Potassium acetate	22.9	3.9- 4.3 [d]

[a] As determined by Wink and Sears (25).

[b] Conditioned in controlled conditions room.

[c] Moisture gained on sorption.

[d] Moisture held on desorption.

Aging chambers were constructed of brass and details of their design are shown in Figure 1. Reflectance disks were stacked up and placed in the chambers as shown. Disks were separated from the brass surfaces on top and bottom by wafers of 0.005-in. teflon. Similar wafers were used to separate the disks of different samples, e.g., those treated with iron and the controls. A minimum of four disks from each sample were placed in the chambers in order that disks coming in contact with the teflon need not be used in the reflectance measurements except as backing.

The oven in which the aging chambers were heated had inside dimensions of 12 by 12 by 12 inches and was fitted with a fan to reduce internal temperature gradients. The temperature of the oven cycled over a 1.5°C. range at 100°C. and completed each cycle in 2-3 minutes.

By sealing a thermocouple in an aging chamber the rate of temperature change in the center of the stack of disks, was determined. It was observed that the disks reached oven temperature in about 30-40 minutes.

After being heated for the desired time interval the chambers were removed from the oven, opened, and the reflectance disks removed. The absorption coefficients of the disks were then redetermined within one hour and the disks analyzed for their metal contents or their intrinsic viscosities.

With the exception of Trials I and XIII, where k was determined as a function of aging time, the terminal absorption coefficient was measured after 42 hours of aging. Thus, for this investigation, the extent of reversion may be defined as the value of k after 42 hours of aging.

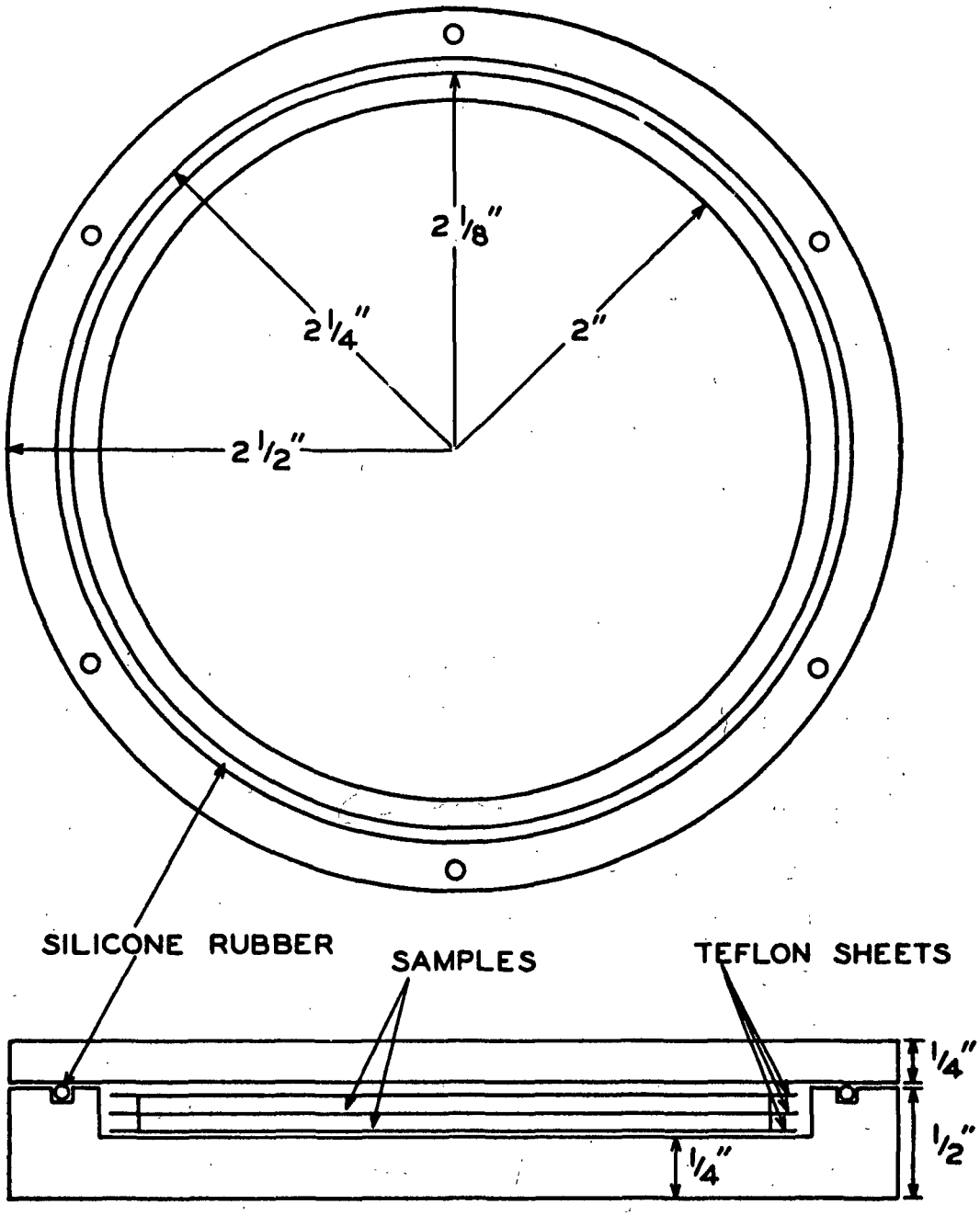


Figure 1. Aging Chambers

DETERMINATION OF METAL TRACES

The amount of metals present on the cotton linters pulp was determined by first destroying the organic portion of a sample of the fibers with concentrated nitric, sulfuric, and perchloric acids, and then measuring colorimetrically the amount of metals in the clear, strongly acidic solution. Iron was determined as the orange-red complex of ferrous ions and 1,10-phenanthroline (26, 27). Manganese was determined as the highly colored permanganate ion which was formed from the lower valence states by oxidation with ammonium persulfate in the presence of a small amount of silver ion catalyst (27). Copper was determined as the orange-brown complex of cuprous ions and 2,9 dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine) (28).

Complete details of the oxidation and metal determinations are given in the APPENDIX, p. 109.

DETERMINATION OF INTRINSIC VISCOSITY

In order to establish the extent to which physical degradation had occurred on aging, the viscosities of the selected samples were measured in 0.5M cupriethylenediamine (Cuene) at a concentration, c, of 0.20 g. cellulose per 100 ml. solution (29, 30). The specific viscosities, η_{sp} were calculated as $(\eta-\eta_o)/\eta_o = \eta_{sp}$, where η is the measured viscosity of the solution and η_o the viscosity of the solvent. Values of the reduced viscosity, η_{sp}/c, were then calculated and used to determine the intrinsic viscosity, $[\eta] = \lim_{c \to 0} (\eta_{sp}/c)$ from charts especially prepared for this purpose (30).

Degrees of polymerization were calculated from intrinsic viscosities by means of the equation, D.P. = $\underline{K}[\eta]$. The value of $\underline{K}$ was taken as 150 as suggested by Gloor and Klug (31).

EXPERIMENTAL RESULTS AND DISCUSSION

The conditions of aging and analytical results for all runs or trials are given in Tables XXVII - XLIV in the APPENDIX, p. 117-37. Different trials are designated by roman numerals in the following discussion.

VARIATION OF ABSORPTION COEFFICIENTS WITH WAVELENGTH

In Trial I the initial absorption coefficient, $\underline{k}_o$, and terminal absorption coefficient, $\underline{k}_{42}$, were measured at various wavelengths in order to determine whether there was an optimum wavelength at which subsequent measurements of $\underline{k}$ should be made. The variation of $\underline{k}_o$ and $\underline{k}_{42}$ with wavelength is shown in Figures 2 and 3. There appears to be no wavelength in the visible region at which these coefficients have a maximum value.

At wavelengths below 440 mmu, differences between $\underline{R}_o$ and $\underline{R}_\infty$ upon which the value of $\underline{k}$ depends were small, and consequently errors in $\underline{k}$ were larger than at higher wavelengths. At wavelengths above 550 mmu, on the other hand, the values of $\underline{k}$ and changes in $\underline{k}$ as a result of aging were very small.

Within the range of 440 - 550 mmu the choice of wavelength for reversion studies appears to be arbitrary. Because brightness is defined as the reflectance at 457 mmu, all reflectance data for calculating absorption coefficients were measured at this wavelength.

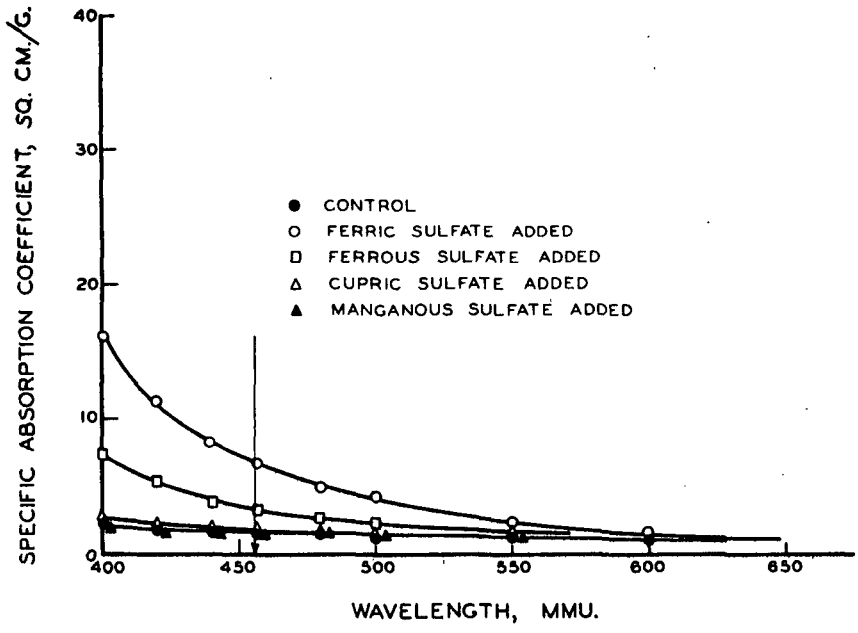


Figure 2. Initial Absorption Coefficient vs. Wavelength

Trial I

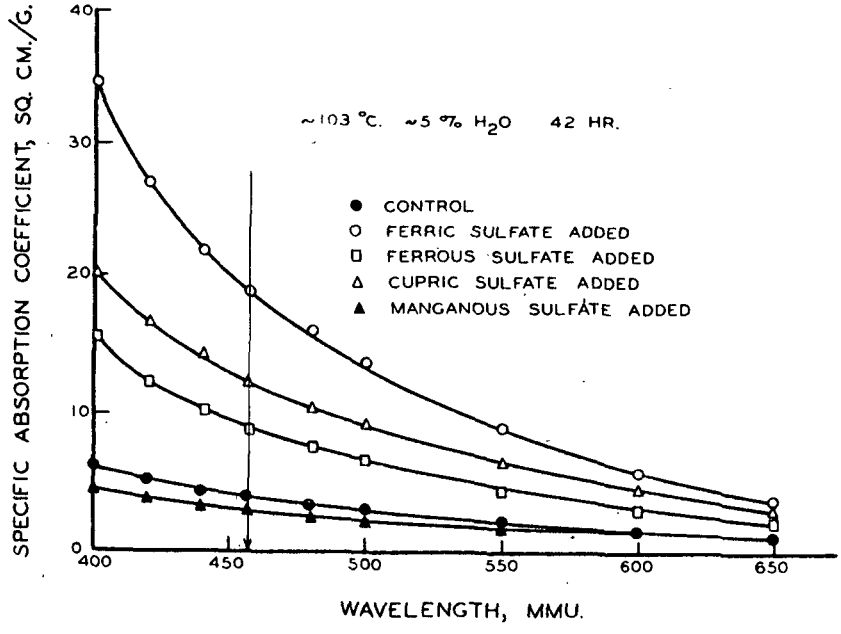


Figure 3. Terminal Absorption Coefficient vs. Wavelength

Trial I

It is apparent from Figures 2 and 3 that metal salts did have an effect on both the initial absorption coefficient, $\underline{k}_o$, and terminal absorption coefficient, $\underline{k}_{42}$, of cotton linters pulp. The presence of ferric or ferrous sulfate caused an appreciable increase in $\underline{k}_o$, while the presence of copper and manganese sulfates caused little change in $\underline{k}_o$. On aging, the iron and copper salts greatly increased the extent of reversion while manganese decreased the extent of reversion relative to the control. Except for the fact that cupric sulfate accelerated reversion more than ferrous sulfate these results are typical of those obtained in all trials.

REPRODUCIBILITY OF ABSORPTION COEFFICIENTS

The reproducibility of absorption coefficients was determined in order to estimate the error in measured values of $\underline{k}$. Data from Trial I were tested by applying the Student "t" distribution (32). For the average value of $\underline{R}_o$ the 95% confidence interval was $\pm$ 0.43 reflectance units, for the average $\underline{R}_\infty$ it was $\pm$ 0.12 reflectance units, and for the average $\underline{k}$ of a sample it was approximately $\pm$ 4.5%.

An analysis of variance for scattering coefficients, $\underline{s}$, determined in Trials II-IVB indicated that no significant differences existed among these coefficients for aged and unaged samples, for control and metal-containing samples, or for samples containing different metals. Very small but significant differences were noted for scattering coefficients determined in different trials. These results indicated

that individual measurements of R_o for all samples were unnecessary for calculating reliable values of k. If for each trial a mean value of s based on 10 measurements was used to determine k from the ratio k/s which had been calculated from R_∞ (See EXPERIMENTAL MATERIALS AND METHODS p. 15), then the 95% confidence interval for the average k of a sample was about ± 5%, or only slightly larger than when k is calculated from individual R_∞ and R_o data.

A comparison of the initial absorption coefficients from Trials I-VIII indicated that the maximum coefficient of variation, i.e., the standard deviation divided by the mean, for k_o was ± 17%. The extent of reversion, or k_{42}, varied with aging conditions and therefore any evaluation of its variation between trials must be based on data from trials in which aging was conducted under nearly identical conditions. A comparison of terminal absorption coefficients from Trials VII, IX, and XIII (105°C. and 4.3% moisture), and Trials VIII, XI, and XII (106°C. and 4.1% moisture) indicated that the maximum coefficient of variation for k_{42} was ± 14%. Any conclusions drawn from comparisons of numerical results from <u>different</u> trials should allow for these variations.

In <u>all</u> trials except two[1] the relative effect of the metal sulfates in promoting reversion was the same: ferric > ferrous > cupric > control > manganous. This fact strongly suggests that the differences in the effects of salts were significant.

[1] In Trials I and III, cupric sulfate caused slightly more reversion than ferrous sulfate.

THE EFFECTS OF METALS ON THE RATE OF REVERSION

In order to determine how metals affect the rate of reversion in cotton linters pulp, the absorption coefficients of reflectance disks were determined after 2, 6, 18, 42, and 66 hours of aging. Results of this experiment (Trial XIII) are shown in Table IV and Figure 4.

The addition of ferric sulfate increased the initial absorption coefficient, k_o, from 1.3 to 4.7 sq. cm./g. while the addition of ferrous sulfate increased k_o to 2.1 sq. cm./g. Copper and manganese salts did not cause a large change in k_o.

During accelerated aging the presence of ferric sulfate greatly increased the extent of reversion for all aging intervals. The presence of ferrous and cupric sulfates did not cause a very great change in the extent of reversion for aging times of less than 18 hours, but did increase the discoloration occurring after longer exposure. Manganese had little effect on reversion at the shorter aging times and, quite unexpectedly, seemed to retard reversion for the longer intervals.

The rate curves in Figure 4 suggest that metal-induced reversion, particularly in the presence of ferric sulfate, occurred as the result of two reactions. The first reaction was an extremely rapid one which appeared to be complete within 2 hours of aging. The second reaction, which appeared to cause the main portion of the discoloration for long aging intervals, proceeded very slowly at first and became increasingly rapid as aging progressed. This reaction showed no signs of approaching completion even after 66 hours of aging.

Since the rate of a chemical reaction is proportional to the concentration of its reactants (33), the reactants of the rapid, short-lived increase in absorption coefficients must have been present in limited quantities and must have been consumed within about 2 hours. It is possible that the reactants in this reaction were either minor constituents of cotton linters pulp or the metal salts. The rate of the slower, second reaction increased with aging time; therefore, its reactants were becoming more abundant with time. In view of the extreme purity of the cotton linters pulp, this observation suggests that the initial precursor of the colored products of this reaction was cellulose itself.

Further significance of the rate at which metal-induced reversion occurred is discussed under EXPERIMENTAL RESULTS, p. 82.

TABLE IV

EFFECT OF ACCELERATED AGING ON THE SPECIFIC ABSORPTION COEFFICIENT

Aging Time[a], hours	Specific Absorption Coefficients, sq. cm./g., of Samples Containing the Following Sulfates:				
	Control	Ferric	Ferrous	Cupric	Manganous
0	1.30	4.70	2.13	1.63	1.27
2	1.90	11.1	3.06	2.36	1.80
6	2.28	12.0	3.86	3.06	2.13
18	3.06	15.8	6.65	5.40	2.48
42	4.76	31.6	23.5	17.7	3.54
66	7.20	64.0	49.8	36.2	5.46

[a] Measured in Trial XIII; aged at 105°C. and 4.3% moisture

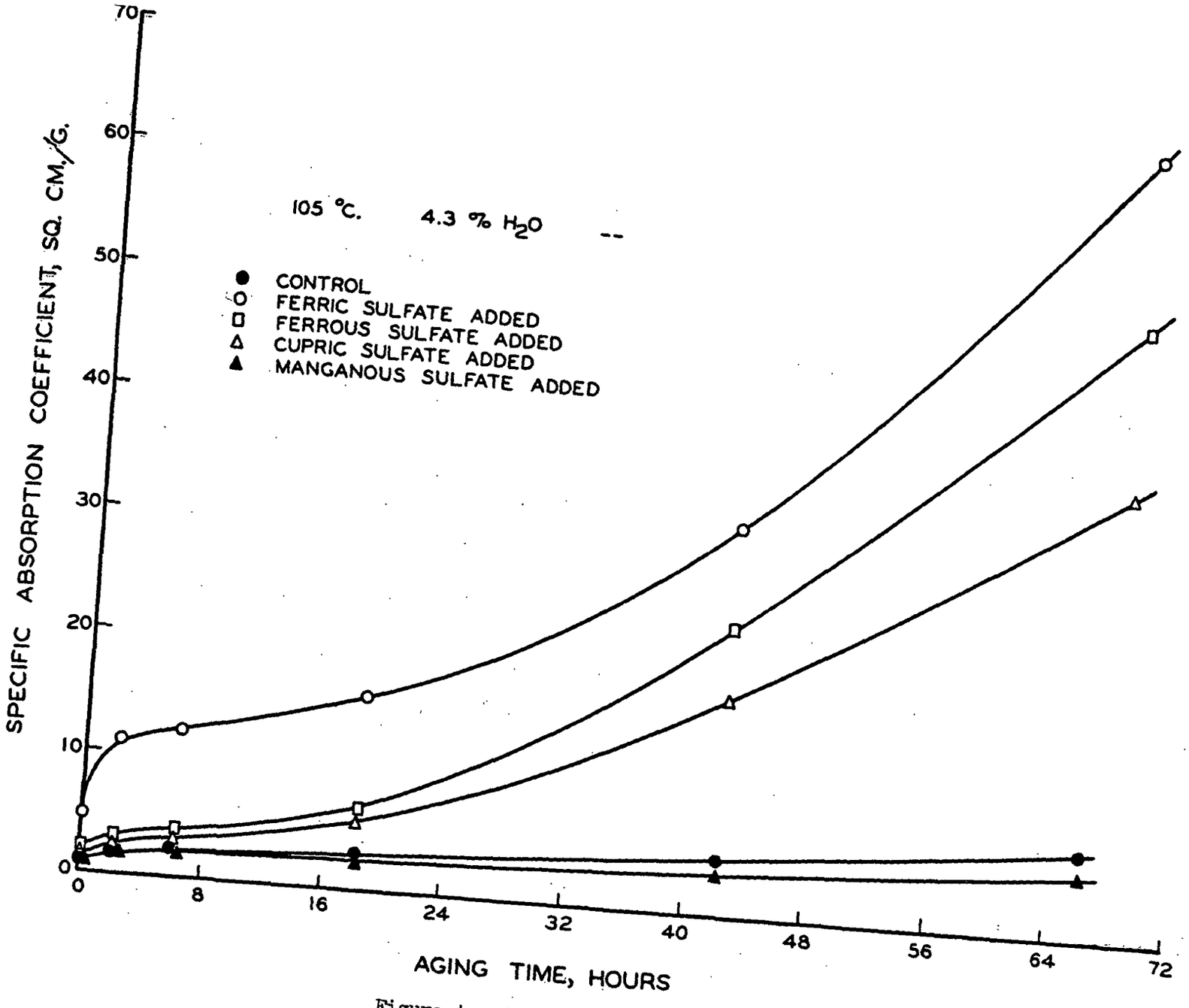


Figure 4. Specific Absorption Coefficient vs. Aging Time

Trial XIII

The order and relative magnitude of the extent to which metal sulfates promoted reversion after 42 hours of aging was as follows:

ferric > ferrous > cupric > control > manganous

6 > 5 > 4 > 1.0 > 0.8

Thus, in comparison to a control containing no added salts, iron and copper accelerated reversion and manganese retarded reversion. In view of these widely differing behaviors it would be useful to review the properties of these four cations. Properties which are likely to be important are summarized in Table V.

The four cations are similar in gross physical and chemical characteristics. All are transition elements and have, with respect to electronic configuration, unfilled 3d orbitals. All cations exhibit similar coordinating properties, each having coordination numbers of either 4 or 6, with 6 being more common for iron and manganese and 4 being more common for copper. The radii of the ions differ somewhat, with ferric ion being the smallest and manganese the largest, but the differences are small.

From the oxidation-reduction potentials shown in Table V it is apparent that cupric and ferric ions tend to act as oxidizing agents, with ferric ion having the greater tendency to be reduced. Ferrous and manganous ions on the other hand are reducing agents, and ferrous ion is more easily oxidized than manganous ion. Thus, two of the detrimental cations are oxidants and one is a reductant, and the beneficial

TABLE V

PROPERTIES OF METAL IONS

Property	Metal Ion			
	Ferric	Ferrous	Cupric	Manganous
Atomic number	26	26	29	25
Atomic weight	55.85	55.85	63.54	54.93
Equivalent weight	18.63	27.93	31.77	27.47
Outer electronic configuration	$3p^6 3d^5$	$3p^6 3d^6$	$3p^6 3d^9$	$3p^6 3d^5$
Number of unshared electrons	5	4	1	5
Coordination number	6	6	4	6
Ionic radius, A (34)	0.67	0.83	0.70	0.91
Redox potentials (35):				
$M^\circ \rightleftharpoons M^{++} + 2e^-$	--	+0.440	-0.345	+1.05
$M^{++} \rightleftharpoons M^{+++} + e^-$	-0.771	--	--	-1.51
$M^{++} \rightleftharpoons M^{++++} + 2e^-$	--	--	--	-1.28
Acid-base properties:				
precipitation pH (35)(36)	2-3	5.5	5.4	8.5
reaction to litmus	acid	acid	sl. acid	neutral
solution pH[a]	3.0[b]	4.8	5.0	5.5
$K_{hyd} = [H^+]^2/c$	$5.6 \times 10^{-4.0}$	$5.6 \times 10^{-7.6}$	$6.4 \times 10^{-8.0}$	$5.5 \times 10^{-9.0}$
Color of oxide (34)	red-black	black	black	gray
Color of hydroxide (34)	red-brown	green	blue	white

[a] Determined for solutions containing 0.1 g. metal per liter.

[b] Turbidity developed at this pH; solution was acidified to pH 2.2 prior to use (see EXPERIMENTAL MATERIALS AND METHODS p. 10).

ion is a reductant. These observations lead one to attach little significance to the ease with which the ions undergo oxidation or reduction in explaining their effects in reversion.

Metal hydroxides other than those of the alkali and alkaline earth metals are weak bases. Accordingly, metal salts of strong acids, such as ferric sulfate, cupric sulfate, etc., hydrolyze to produce acidic solutions according to the reaction (33):

$$M^+ + 2H_2O \rightleftharpoons MOH + H_3O^+$$

For this reaction it may be shown that

$$K_{hyd} = \frac{[H_3O^+]\,[MOH]}{[M^+]} = \frac{Kw}{Kb}$$

where K_w and K_b are the ionization constants for water and the metal hydroxide, respectively. The extreme insolubility of the metal hydroxides, however, makes the rigorous evaluation of the hydrolysis constant, K_{hyd}, or K_b difficult.

Approximate evaluation of K_{hyd} can be accomplished with pH measurements of salt solutions of known concentration and the following relationship derived for solutions of salts of weak bases and strong acids (33):

$$[H^+] = \sqrt{K_{hyd}\, c} \text{ or } K_{hyd} = [H^+]^2/c.$$

The apparent correlation between the ability of the metals to accelerate reversion and their tendency to hydrolyze in solution

suggests that the products of hydrolysis, i.e., metal hydroxides and free acids, may play a significant role in the discoloration of cotton linters containing metal salts.

The last property of the metal ions to be considered in Table V is the color of their hydroxides. If indeed the metal salts do hydrolyze before or during aging, then some metal hydroxides will be precipitated on the fibers. If, furthermore, these hydroxides are colored they may be responsible for a portion of reversion caused by metal salts. The colors of hydroxides are shown in Table V. Ferric hydroxide is red-brown while ferrous hydroxide is a pale green, cupric hydroxide blue, and manganous hydroxide white. Referring to Figure 4 it is interesting to note that it was ferric sulfate which caused the greatest increase in $\underline{k}$ after two hours of aging, while ferrous and cupric sulfates had only small effects, and manganous sulfate had virtually no effect on $\underline{k}$ during the same interval. This observation suggests that the color of the hydroxides may be partially responsible for initial discoloration and reversion occurring during the first two hours of aging.

In order to test the hypothesis that ionic acidity (basicity) is a factor in metal-induced reversion, the effects of aluminum, lanthanum, cadmium, and magnesium were checked. The properties of these metals are summarized in Table VI. Cadmium, lanthanum, and magnesium are quite strongly basic having precipitation pH values of 7.5 and greater. Aluminum, on the other hand, is much more acidic having

TABLE VI

PROPERTIES OF METAL IONS

Property	Metal Ion			
	Aluminum	Cadmium	Lanthanum	Magnesium
Atomic number	13	48	57	12
Atomic weight	26.98	112.41	138.92	24.32
Equivalent weight	8.99	56.21	46.31	12.16
Outer electronic configuration	$2s^2 2p^6$	$4d^8 5s^2$	$5s^2 5p^6$	$2s^2 2p^6$
No. of unshared electrons	0	2	0	0
Coordination number	6	4	6	4
Ionic radius, A (34):	0.57	1.03	1.22	0.78
Redox potentials (35):				
$M^\circ = M^{++} + 2e^-$	—	+0.402	—	+2.34
$M^\circ = M^{+++} + 3e^-$	-1.67	—	+2.37	—
Acid-base properties:				
precipitation pH (35)(36)	4.0	7.5	8.2	10.5
reaction to litmus	acid	neutral	—	sl. alkaline
solution pH	3.9[a]	5.3	—	8.6[b]
$K_{hyd} = [H^+]^2/c$	$2.7 \times 10^{-5.8}$	$5.6 \times 10^{-8.6}$	—	$5.6 \times 10^{-15.2}$
Color of oxide (34)	white	brown	white	white
Color of hydroxide (34)	white	white	—	white

[a] Determined for solutions containing 0.00372 gram atoms of metal per liter.

[b] Determined for solutions containing 0.00180 gram atoms of metal per liter.

Table VII

EFFECTS OF Cd, La, Mg, AND Al ON DISCOLORATION

Aging Time, hours	Moisture Content,%	Specific Absorption Coefficients, sq. cm./g., of Samples Containing the Following Sulfates:					
		Control	Fe^{+++}	Cd^{++}	La^{+++}	Mn^{++}	Mg^{++}
0[a]	--	1.33	4.62	1.17	1.30	1.30	1.31
42[a]	4.1	6.05	42.8	4.63	4.57	3.79	4.57
42[a]	7.0	5.00	27.2	4.93	4.45	3.14	4.69
		Control	Fe^{+++}	Al^{+++}			
0[b]	--	1.26	4.63	1.16			
42[b]	4.0	3.95	30.2	4.87			

[a] Measured in Trial XI; aged at 106°C. The effects of Cd, La, and Mg were checked again in Trial XIVC and similar results were obtained.

[b] Measured in Trial XIVB; aged at 105°C.

a precipitation pH of 4.0 or only slightly higher than that for ferric iron.

As shown in Table VII the addition of cadmium, lanthanum, or magnesium sulfates resulted in small but detectable improvements in the color stability of cotton linters. These salts were about equally effective in retarding reversion, but less so than manganous sulfate. The addition of aluminum sulfate appeared to accelerate reversion only slightly.

The results obtained for cadmium, lanthanum, and magnesium tend to support the hypothesis that the ease with which metal salts hydrolyze is associated with their ability to accelerate reversion. The result observed for aluminum, which has an acidity between those for ferric and ferrous iron, however, does not support this hypothesis.

THE EFFECTS OF MOISTURE AND TEMPERATURE

MOISTURE

In the course of reproducing values of the terminal absorption coefficient it was discovered that the moisture content of samples during aging had an effect on reversion. Experiments were therefore conducted to determine the importance of this moisture effect. The moisture contents of reflectance disks were adjusted to approximately 4, 7, 10, or 11% by conditioning them over saturated salt solutions (see EXPERIMENTAL MATERIALS AND METHODS, p. 16). Samples for each moisture content were sealed in separate aging chambers prior to heating. For aging in the absence of moisture, i.e., 0% moisture, unconditioned reflectance disks were placed in aging chambers which were not tightly sealed. All samples were aged simultaneously in order to cancel out variation due to temperature differences. After 42 hours of aging the samples were removed from the chambers and their terminal absorption coefficients measured.

The effects of moisture are summarized for two aging temperatures in Table VIII. The results are qualitatively similar at both 100 and

107°C., but at the higher temperature the effects of moisture are much more pronounced. Results of Trial VI are shown in Figure 5.

Some reversion occurred at all moisture levels for all samples. However, the extent of reversion for samples containing ferric, ferrous and cupric sulfates had an apparent maximum at 4.1% moisture. Although there are insufficient data to determine the exact position of this maximum, there can be little doubt that one occurred between 0 and 7% moisture. Such a maximum for the control and the manganese-containing sample was much less distinct than for the other samples.

These results were totally unexpected in view of the findings reported by other investigators. Tongren (38), McIntyre (39), and Rollinson (1) working with a variety of bleached wood pulps, found that the rate of reversion at approximately 100°C. increased as the relative humidity was increased from 0 to 90% R.H. during aging. McIntyre (39), moreover, noted that his particular Mitscherlich pulp exhibited a minimum reversion rate at about 20% R.H. None of these investigators reported a relative humidity at which reversion had a maximum rate. It is not clear whether this discrepancy is due to differences in materials, i.e. cotton linters vs. wood pulp, or the experimental conditions during aging, i.e., sealed chambers vs. open oven.

Several investigators (37), however, have observed that nonenzymatic browning in dehydrated foods increases and passes through a maximum as the water content of the foods is increased. If metal-induced

TABLE VIII

EFFECT OF MOISTURE ON DISCOLORATION

Aging No., Time, hours	Moisture Content, %	Specific Absorption Coefficients, sq. cm./g., of Samples Containing the Following Sulfates:				
		Control	Ferric	Ferrous	Cupric	Manganous
0[a]	--	1.50	5.42	2.48	1.64	1.48
42	0	2.87	8.55	4.93	4.23	3.39
42	4.1	5.04	15.1	9.48	9.17	3.93
42	7.1	5.45	11.5	7.55	7.34	3.47
42	10.1	4.77	10.3	7.08	5.02	4.15
42	11.3	4.77	9.90	7.72	5.51	3.74
0[b]	--	1.45	4.79	2.09	1.70	1.58
42	0	2.92	7.19	4.30	3.20	3.44
42	4.2	7.20	48.0	42.0	29.8	5.67
42	6.9	6.33	18.2	13.5	13.6	3.61
42	9.4	6.40	13.4	10.7	9.40	4.23
42	11.4	5.76	11.5	7.88	5.94	4.44

[a] Measured in Trial V; aged at 100°C.

[b] Measured in Trial VI; aged at 107°C.

reversion is analogous to this system, the occurrence of a maximum in the moisture vs. reversion curve is not surprising.

TEMPERATURE

Another aging variable found to be important in reversion was temperature. The absorption coefficient of cotton linters pulp, either with or without added metals, was observed to increase from its initial or unaged value by a factor of roughly 3 upon being aged 42 hours at 100°C. At slightly higher temperatures, however, the extent of reversion was much greater.

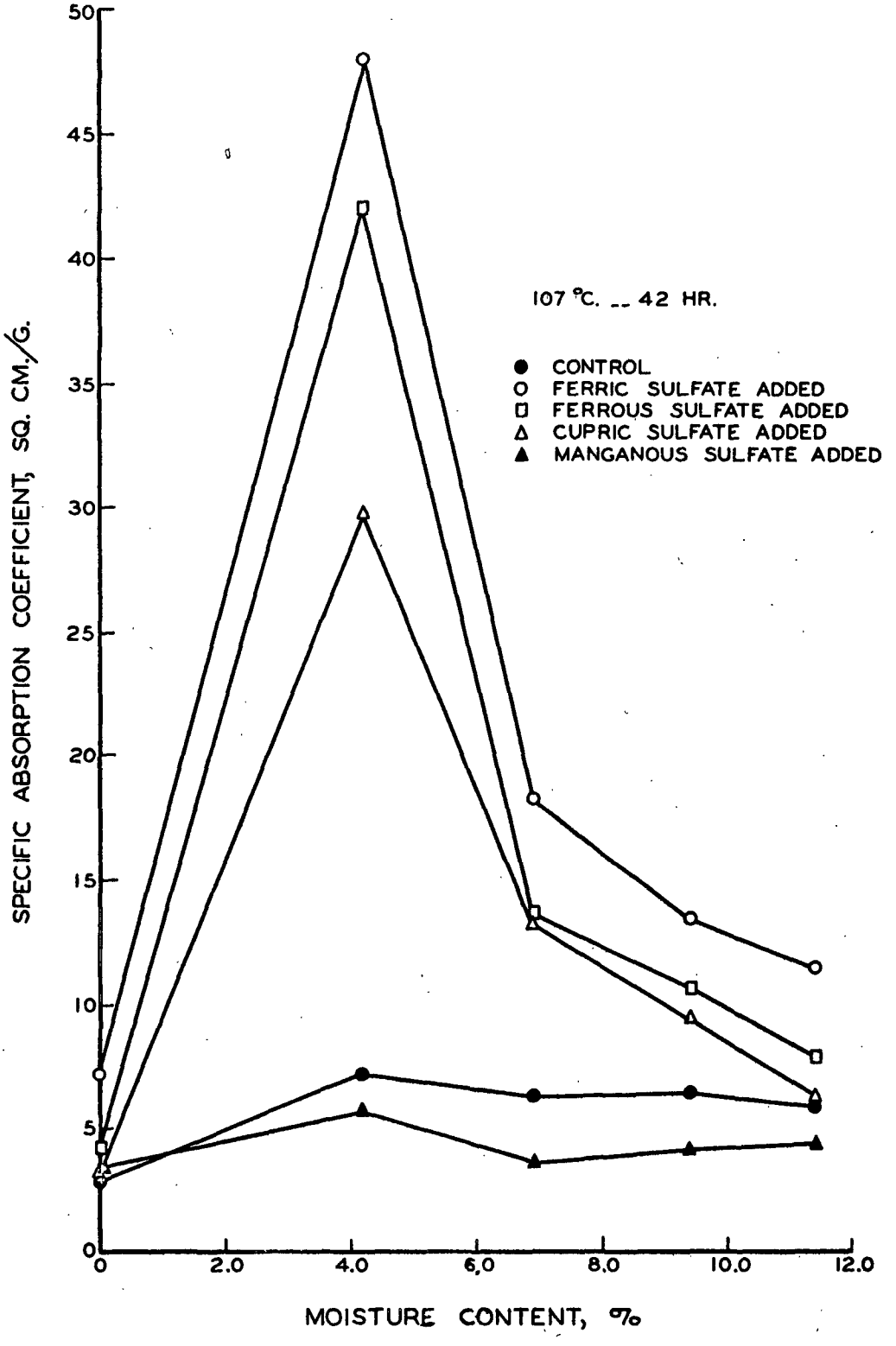


Figure 5. Specific Absorption Coefficient vs. Moisture Content

Trial VI

In order to estimate the effect of temperature on the extent of reversion, reflectance disks prepared in the usual way were conditioned at 22.9% R.H. to a moisture content of 4% and aged at different temperatures.

Practical difficulties encountered in controlling the oven temperature place some doubt on the absolute accuracy of the recorded temperatures. Their relative values, however, should be correct.

Values of the absorption coefficient after 42 hours of aging at the various temperatures are shown in Table IX and Figure 6. In this figure the points at 25°C. are for values of $\underline{k}$ prior to aging.

From Figure 6 the extreme temperature sensitivity of metal-induced reversion is readily apparent. The extent of reversion for samples of cotton linters containing iron and copper salts approximately doubled for a 5 degree increase in temperature in the range 100-107°C. For samples containing manganese salts or the control, the extent of reversion did not quite double in the range 100-107°C. Extrapolation of the temperature curves for these samples suggests that a 10° change would have been required for a doubling of their rates of reversion.

These results suggest that variation in terminal absorption coefficients from different trials could be due to small temperature differences. If this is the case, temperature control would be of paramount importance in any attempt to reproduce terminal absorption coefficients accurately.

TABLE IX

EFFECT OF TEMPERATURE ON DISCOLORATION

Trial No.	Aging Temp.,[a] °C.	Moisture Content, %	Specific Absorption Coefficients, sq. cm./g. of Samples Containing the Following Sulfates:				
			Control	Ferric	Ferrous	Cupric	Manganous
V	25	--	1.50	5.42	2.48	1.64	1.48
V	100	4.1	5.04	15.1	9.48	9.17	3.93
VII	105	4.3	5.36	29.5	25.7	15.5	3.63
VIII	106	4.2	6.51	39.2	33.8	25.9	4.76
VI	107	4.2	7.20	48.0	42.0	29.8	5.67

[a] All samples were aged 42 hours.

Other investigators have found reversion rates to be temperature sensitive. Thus, Tongren (38) observed that the rate of reversion of a bleached sulfite pulp tripled for a 20° increase in temperature in the range 70-110°C. Giertz (40) found that aging for 72 hours at 100°C. gave the same degree of yellowing in a variety of wood pulps as aging for 16 hours at 120°C. This suggests that the rate of reversion increases by a factor of 4-1/2 for each 20°C increase in temperature. The effect of temperature noted in this investigation for the control and the sample containing manganous sulfate is in approximate agreement with the results of Giertz, i.e., reversion doubles for a 10°C. increase in aging temperature. The sensitivity of iron- and copper-containing samples, on the other hand, is far greater than that noted by Tongren or Giertz for any pulp.

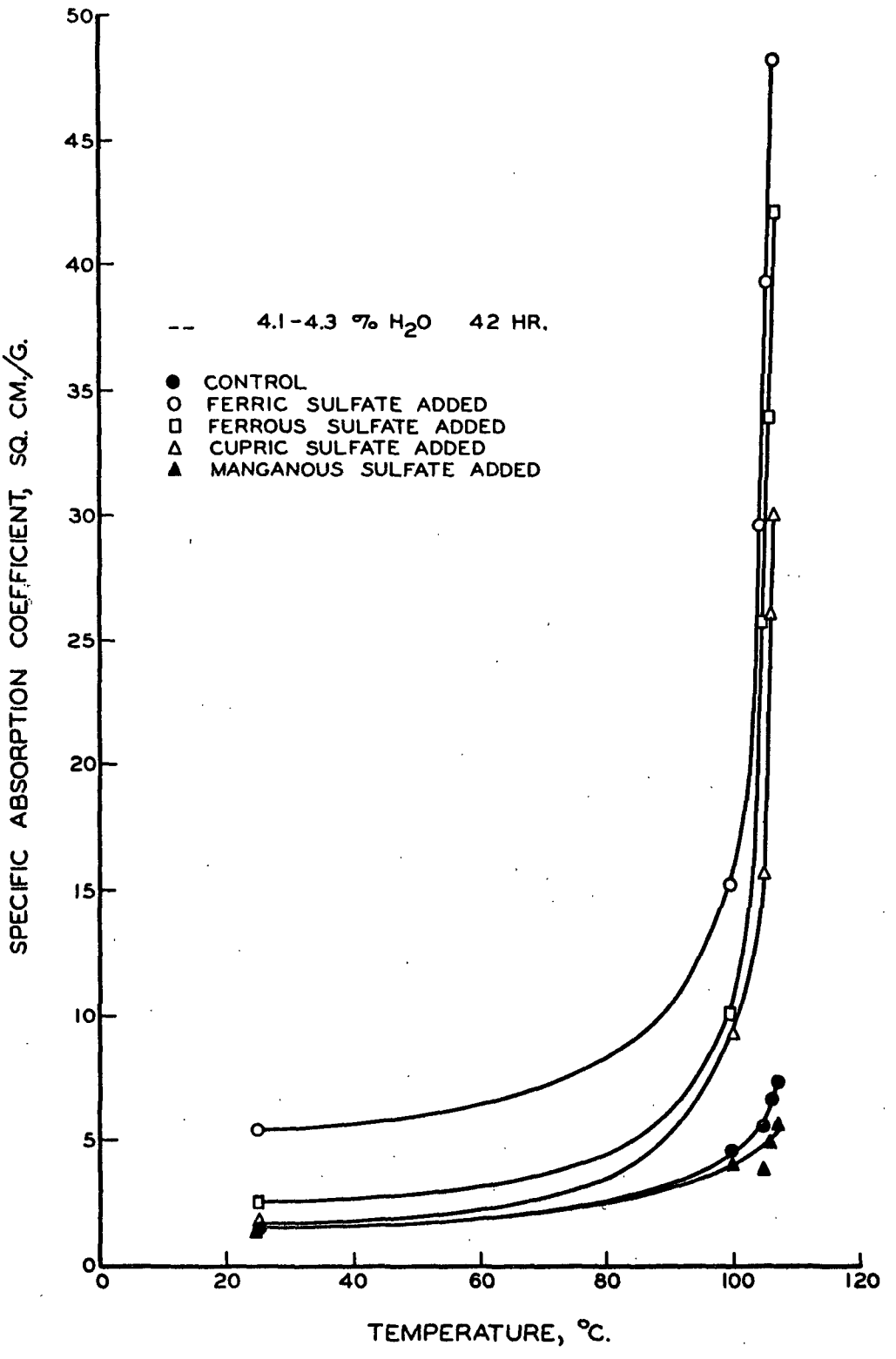


Figure 6. Specific Absorption Coefficient vs. Temperature

Trials V-VIII

THE EFFECTS OF ANIONS, METAL CONCENTRATION, AND HYDROGEN-ION CONCENTRATION

ANIONS

Since the effects of the metal salts might not have been independent of their acid radicals, experiments were undertaken in Trials II, VII, and XIVB to compare the effects of sulfate, chloride, and acetate salts.

Reflectance disks were prepared as usual except that different metal salt solutions were used. The hydrogen-ion concentrations of the salt solutions are shown in Table X. The disks were conditioned at 22.9% R.H. to a moisture content of 4% and aged simultaneously in each trial to cancel temperature variations.

The results of Trials II, VII, and XIVB are shown in Table XI. For manganous, cupric, and ferrous salts there were no significant differences in the absorption coefficient before aging, $\underline{k}_o$, or the absorption coefficient after aging, $\underline{k}_{42}$, for the three anions. This would indicate that the effects observed for these salts are due specifically to the presence of the cations rather than anions.

For ferric salts, on the other hand, the chloride and acetate, solutions of which were darker than the water-white sulfate solution, caused larger increases in $\underline{k}_o$ and $\underline{k}_{42}$ than the sulfate. Moreover, the magnitude of these differences was the same whether unacidified (Trial VII) or acidified (Trial XIVB) solutions of the chloride and

TABLE X

THE pH OF SALT SOLUTIONS

Trial	Anions	Cations[a]			
		Ferric	Ferrous	Cupric	Manganous
All except VII	Sulfates	2.2[b]	2.2[c]	5.0	5.5
VII	Sulfates	2.2[b]	4.8	5.0	5.5
	Chlorides	3.0	4.7	5.0	5.5
	Acetates	4.0	--	6.0	6.2
XIVB	Sulfates	2.2[b]	--	--	--
	Chlorides	2.1[d]	--	--	--
	Acetates	2.1[e]	--	--	--

[a] The concentration of all solutions was 0.1 g. metal per liter.

[b] These solutions were acidified from a pH of 3.0 with sulfuric acid to prevent the formation of colloidal hydroxides.

[c] This solution was acidified from a pH of 4.8 with sulfuric acid to prevent the formation of colloidal hydroxides.

[d] This solution was acidified from a pH of 3.0 with hydrochloric acid.

[e] This solution was acidified from a pH of 4.0 with acetic acid.

acetate were used. In addition, the metal contents of samples containing the chloride and acetate were four to five times greater than that of the sulfate sample (see Table XII, p. 45).

METAL CONCENTRATION

In an attempt to find out how metal-induced reversion varied with metal concentration, reflectance pads were made up from slurries to which 0.5, 1.0, and 5.0 p.p.m. of metal had been added. These disks

TABLE XI

EFFECT OF ANIONS ON DISCOLORATION

Aging Time, hours	Anions	Specific Absorption Coefficient, sq. cm./g., of Samples Containing the Following Salts: Control	Ferric	Ferrous	Cupric	Manganous
0[a]	Sulfate	1.52	4.93	2.24	1.58	1.54
0	Chloride	1.52	28.4	2.85	1.69	1.69
0	Acetate	1.48	14.6	--	1.58	1.47
42[a]	Sulfate	5.36	29.5	25.7	15.5	3.63
42	Chloride	3.82	42.1	24.3	13.8	3.29
42	Acetate	4.06	31.6	--	14.2	3.01
42[b]	Sulfate	2.86	--	--	5.61	--
42	Chloride	--	--	--	6.29	--
42	Acetate	--	--	--	5.28	--
0[c]	Sulfate	1.26	4.51	--	--	--
0	Chloride	--	26.8	--	--	--
0	Acetate	--	17.6	--	--	--
42[c]	Sulfate	3.95	27.2	--	--	--
42	Chloride	--	42.8	--	--	--
42	Acetate	--	31.0	--	--	--

[a] Measured in Trial VII; aged at 105°C. and 4.3% moisture.

[b] Measured in Trial II; aged at about 100°C.

[c] Measured in Trial XIVB; aged at 105°C. and 4.0% moisture.

were conditioned at 22.9% R.H. and aged together. After the disks were aged their terminal absorption coefficients were measured and their metal contents determined chemically. The results of these analyses as well as the results of metal analyses from Trials II-VII are shown in Table XII.

TABLE XII

RETENTION OF METALS BY COTTON LINTERS

Trial	Slurry Concentration, p.p.m.	Metal Retained, microgram-atoms/g. pulp, From Slurries Containing the Following Sulfates: Ferric	Ferrous	Cupric	Manganous
II	1.0	- -	- -	1.35	- -
	1.0	- -	- -	0.91	- -
	1.0	- -	- -	1.03	- -
	1.0	- -	- -	0.98	- -
III	1.0	1.81	0.84	1.18	1.26
IVA	1.0	1.51	0.76	1.41	1.14
	1.0	1.50	0.69	1.44	1.21
IVB	1.0	- -	- -	1.32	0.73
	1.0	- -	- -	1.32	0.78
	1.0	- -	- -	1.28	0.70
V	1.0	1.44	0.65	1.16	0.82
VI	1.0	1.54	0.63	1.14	1.19
VII	1.0	1.53	1.15[a]	1.24	0.94
	1.0[c]	6.58[b]	1.11[a]	1.22	0.93
	1.0[d]	5.29[b]	- -	1.26	1.09
VIII	0.5	1.56	0.69	0.82	0.91
	1.0	1.38	0.59	1.11	0.85
	5.0	1.04	0.45	1.27	1.02
	Av.	1.54	0.65	1.18	0.95

[a] The pH of these metal salt solutions was 4.8 and 4.7 instead of 2.2 as it was for all other samples. These retention values are not included in the average.

[b] The pH of these metal salt solutions was 3.0 and 4.0 instead of 2.2 as it was for all other samples. These retention values are not included in the average.

[c] Chloride salts.

[d] Acetate salts.

It is apparent that the amounts of metal retained in all trials fell within fairly narrow limits even when, as in Trial VIII, the metal concentration of the slurry was varied tenfold. Notable exceptions to this generalization are the ferric acetate and chloride of Trial VII, and the ferrous sulfate and chloride of Trial VII whose solutions were slightly more alkaline than the ferrous sulfate solution used throughout the rest of the investigation.

The absorption coefficients of samples for Trial VIII are given in Table XIII. Metal concentrations in the slurries had no measurable effect on the extent of metal-induced reversion. This is not surprising in view of the fact that the amount of metal retained was nearly the same for all slurry concentrations.

HYDROGEN-ION CONCENTRATION

In discussing the effect of hydrogen-ion concentration on reversion, distinction must be made between the hydrogen-ion concentrations of:

1. The metal salt solutions added to the pulp slurries,
2. The slurries from which the reflectance pads are made, and
3. the reflectance disks themselves.

The first of these, the hydrogen-ion concentrations of the salt solutions, varied considerably from metal to metal because of the varying degree to which the salts hydrolyze and because of the need for acidification of iron sulfate solutions to prevent precipitation of colloidal hydroxides. As summarized earlier in Table II, the pH of the salt

TABLE XIII

EFFECT OF SLURRY CONCENTRATION ON DISCOLORATION

Aging Time,[a] hrs.	Slurry Concentration, p.p.m.	Specific Absorption Coefficients, sq. cm./g., of Samples Containing the Following Sulfates:				
		Control	Ferric	Ferrous	Cupric	Manganous
0	0.5	1.33	4.27	2.20	1.84	1.56
0	1.0	1.28	4.50	2.37	1.70	1.31
0	5.0	1.24	3.41	1.93	1.42	1.30
42	0.5	5.56	37.2	32.2	21.1	4.13
42	1.0	6.51	39.2	33.8	25.9	4.76
42	5.0	5.84	37.6	27.9	25.3	4.07

[a] Measured in Trial VIII; aged at 106°C. and 4.2% moisture.

solutions varied from 2.2 for iron sulfates to about 5.5 for manganous sulfate and water itself. This variation, however, was not reflected very greatly in the pH of the pulp slurries to which the solutions were added. This was true because not more than 20 cc. of the salt solutions were added to 2000 cc. of slurry. Thus, the slurries containing no metal had pH's of 5.0-5.5, and those containing 20 cc. of the acidified iron sulfate solutions had pH's of 4.0-4.5.

In order to see whether this difference in hydrogen-ion concentration of the slurries could be responsible for the detrimental effects noted for iron salts, reflectance disks were prepared from metal-free slurries that had been acidified to pH 4.0 with sulfuric acid, and from metal-free slurries that had not been acidified and had a pH of about 5.5. These two sets of samples, with other samples from Trial IVA, were conditioned

to 5.2% moisture and aged at about 100°C. for 42 hours. The absorption coefficient of the unacidified sample increased from 1.43 to 4.51 sq. cm./g. during aging and that of the acidified sample increased from 1.44 to 3.85 sq. cm./g. The difference between the extent of reversion for these samples is not significant, indicating that small differences in slurry pH arising from the addition of metal salt solutions were not alone responsible for the greater discoloration produced by iron salts. Results leading to the same conclusion were obtained with ferrous sulfate-containing disks which had been made from slurries with pH's of approximately 4.2 and 5.8. The absorption coefficient of disks prepared at a pH of 4.2 increased from 1.90 to 24.5 sq. cm./g. during aging at 4.2% moisture and 105°C. (Trial IX), while the absorption coefficient of the disks prepared at a pH of 5.8 increased from 2.24 to 25.7 sq. cm./g. under the same aging conditions (Trial VII).

The third hydrogen-ion concentration to consider, namely that of the reflectance disks themselves, is probably of greatest fundamental importance because it is at this concentration that aging actually occurs. This concentration undoubtedly varies from sample to sample, if for no other reason than the fact that the salts of different metals hydrolyze to different degrees on heating. Indeed this may be an important aspect of metal-induced reversion. Direct verification of this hypothesis, however, would require a measurement of the hydrogen-ion concentration in the reflectance disks under the conditions of aging. Unfortunately, the means for making such a measurement are not readily available.

In an attempt to ascertain whether the maximum amount of acid which could be released by salt hydrolysis would cause noticeable discoloration, 2.3 micromoles of sulfuric acid per gram of cotton linters were added to reflectance disks previously prepared as controls, i.e., free of added metal salts. The choice of 2.3 micromoles of acid was based on the fact that samples treated with ferric sulfate had been observed to retain, on the average, 1.5 microgram-atoms of iron per gram (see EXPERIMENTAL RESULTS, p. 43-6); and the assumption that all of the metal had been sorbed as the sulfate and had undergone complete hydrolysis during aging.

The acid was added to the disks in a sufficient total volume (2-3 ml.), to wet them completely, and the disks were then air dried without being pressed so that no acid would be removed. After the k_o of these disks had been determined, they were conditioned 24 hours at 22.9% R.H. and then aged 42 hours together with a control and a sample containing ferric sulfate. Results of this experiment are shown in Table XIV.

The aged, acid-containing disks were atypical in having a dark band at the periphery of each disk. The terminal absorption coefficients, k_{42}, derived from the more uniformly colored interior areas, do not, therefore, represent all of the pigment formed. Hence, the following comparison is indicative rather than strictly quantitative.

Allowing for the discoloration (approximately 10 sq. cm./g.) believed to be due to inorganic compounds in samples containing ferric sulfate (see EXPERIMENTAL RESULTS, p. 51), the acid equivalent of 1.5 microgram-atoms of ferric iron could account for at least one half of the

organic color (approximately 20 sq. cm./g.) developed in the presence of this amount of iron.

For the above experiment it was assumed that all of the metal had been sorbed as the sulfate. As a check, the control and the sample containing ferric sulfate were analyzed for sulfur by two methods:

a. iodimetric determination of sulfur dioxide evolved during high temperature combustion, and

b. micrograviметric determination of sulfate as barium sulfate.

The results of these analyses are given in Table XV.

TABLE XIV.

EFFECT OF SULFURIC ACID ON DISCOLORATION

Aging Time,[a] hours	Specific Absorption Coefficients, sq. cm./g., of the Following Samples:		
	Control	Sulfuric Acid Added[b]	Ferric Sulfate Added[c]
0	1.26	1.30	4.63
42	3.95	10.7	30.2
42[d]	3.95	10.7	~20

[a] Measured in Trial XIVB; aged at 105°C. and 4.0% moisture.

[b] Each disk contained 2.3 micromoles of sulfuric acid per gram of linters.

[c] Each disk is estimated to have contained 1.5 microgram-atoms of iron per gram of linters.

[d] Adjusted for discoloration due to iron compounds.

Obviously, the data are insufficient to warrant a definite conclusion, but it appears that less than half of the iron had been sorbed as ferric sulfate.

THE CONTRIBUTION OF INORGANIC COMPOUNDS TO REVERSION

It was suggested in the analysis of this problem that metals could cause discoloration in cotton linters pulp either by forming colored inorganic materials or by promoting the formation of colored organic materials. This experiment was undertaken, therefore, to establish the extent to which inorganic compounds contribute to the color of aged cotton linters pulp.

Reflectance disks were prepared and their initial absorption coefficients and metal contents determined. Two disks from each sample were separately extracted with 125 ml. of a dilute acid mixture (0.1N in hydrochloric acid and 0.1N in hydrofluoric acid) on a sintered glass filter funnel for 2-4 minutes. The extracted disks were pressed and dried according to the procedure used for forming reflectance pads, and their absorption coefficients redetermined.

Two groups of four additional disks from each sample were conditioned at 22.9% R.H. to a moisture content of about 4% and aged. One group was aged 2 hours and the other group 42 hours. The terminal absorption coefficients of these aged disks were measured and the disks then extracted in the same manner as the unaged samples. Absorption coefficients and metal

TABLE XV

RESULTS OF SULFUR ANALYSES

Sample		Sulfate Content, micromoles/g. Based on the:		
		Combustion Method[a]	Micrograviметric Method[b]	Iron Content[c]
Ferric sulfate added		0.66	0.52	—
		1.06	1.06	—
		3.45	—	—
	average	1.72	0.79	2.3
Control		0.77	0.38	—
		2.04	—	—
		0.41	—	—
	average	1.07	0.38	—
	difference	0.65	0.41	2.3

[a] Weighed specimens (0.5-1.0 g.) of each sample were ignited in a stream of oxygen to a maximum temperature of 2800°F. in a Leco induction furnace. The evolved sulfur dioxide was automatically titrated with potassium iodate in the presence of starch indicator, potassium iodide, and hydrochloric acid.

[b] Ten gram specimens of each sample were neutralized with 10 mg. of sodium carbonate and ashed. The ash residue was leached with water, and the soluble sulfate precipitated with barium chloride. The precipitate was permitted to digest overnight before being filtered, ignited, and weighed as barium sulfate.

[c] Estimated to be 1.5 microgram-atoms of iron per gram of linters; this corresponds to approximately 2.3 micromoles of sulfate per gram of linters.

contents of these aged and extracted samples were then carefully redetermined. The collected data are shown in Tables XVI and XVII and Figure 7, 8, 9, and 10.

The acid extraction restored the absorption coefficients of all unaged, metal-containing disks to the value of the unaged, metal-free control. This suggests that increases in k_o are probably due entirely to the retention of colored metallic compounds.

Acid extraction of the samples which had been aged 2 hours restored their absorption coefficients to values only slightly higher than that for the control. It therefore appears that increases occurring in k during the first two hours of aging are largely due to the formation of colored metallic compounds.

Acid extraction of samples which had been aged 42 hours, on the other hand, reduced their absorption coefficients only 24-38%. Since k is proportional to the chromophore concentration this result may be interpreted as meaning that 24-38% of the materials absorbing light at 457 mmu were removed.

The metal content of samples before and after extraction are shown in Table XVII and Figure 10. It may be seen that the acid extraction removed 84 to 100% of the added metals from the disks aged 42 hours. Thus, acid extraction, while removing only 24 to 38% of the total amount of materials absorbing light at 457 mmu, removed 84 to 100% of the added metals. In other words 62 to 76% of the color-producing materials in samples which had been aged 42 hours were insoluble whereas only 0 to 15% of the metals were insoluble.

A precise distinction between organic and inorganic color in samples

TABLE XVI

EFFECT OF ACID EXTRACTION ON DISCOLORATION

Sample	Specific Absorption Coefficients, sq. cm./g., of Samples Containing the Following Sulfates:				
	Control	Ferric	Ferrous	Cupric	Manganous
Unaged, unext'd.[a]	1.45	4.50	2.36	1.80	1.51
Unaged, ext'd.	1.40	1.49	1.46	1.37	1.43
difference	0.05	3.01	0.90	0.43	0.08
difference, %[d]	3.4	66.9	38.2	23.9	5.3
Aged, 2 hrs., unext'd.[b]	1.75	9.81	3.04	2.12	1.69
Aged, 2 hrs., ext'd.	1.66	1.89	1.82	1.86	1.72
difference	0.09	7.92	1.22	0.26	--
difference, %[d]	5.1	80.8	40.1	12.3	--
Aged, 42 hrs., unext'd.[c]	5.56	34.2	29.7	21.7	4.21
Aged, 42 hrs., ext'd.	3.97	21.0	19.0	14.4	3.21
difference	1.59	13.2	10.7	7.3	1.00
difference, %[d]	28.6	38.6	36.0	33.6	23.8

[a] Measured in Trial X.

[b] Measured in Trial XIVA; aged at 4.0% moisture and 105°C. for two hours.

[c] Measured in Trial X; aged at 4.2% moisture and 106°C. for 42 hours.

[d] % Difference = (Difference x 100)/unext'd.

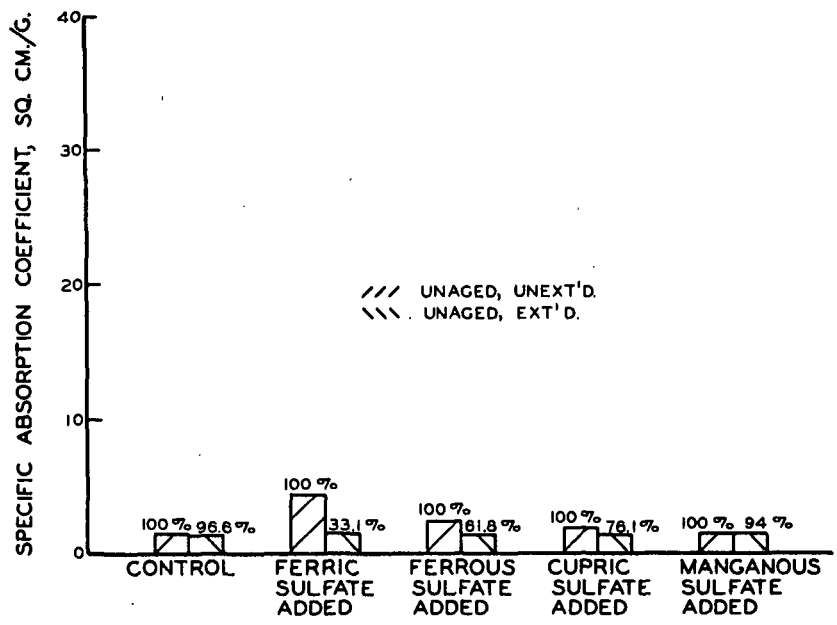


Figure 7. Effect of Acid Extraction on the Specific Absorption Coefficient of Unaged Samples

Trial X

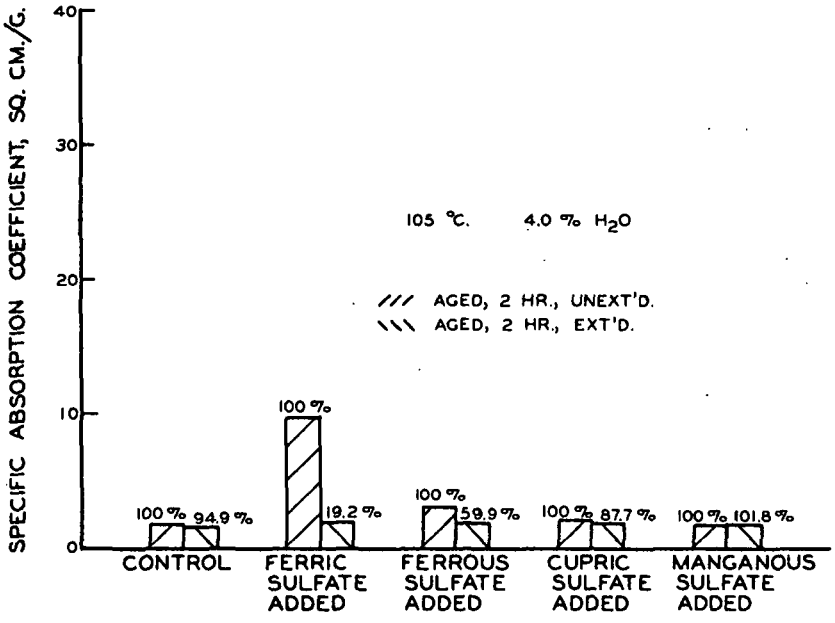


Figure 8. Effect of Acid Extraction on the Specific Absorption Coefficient of Aged Samples

Trial XIV

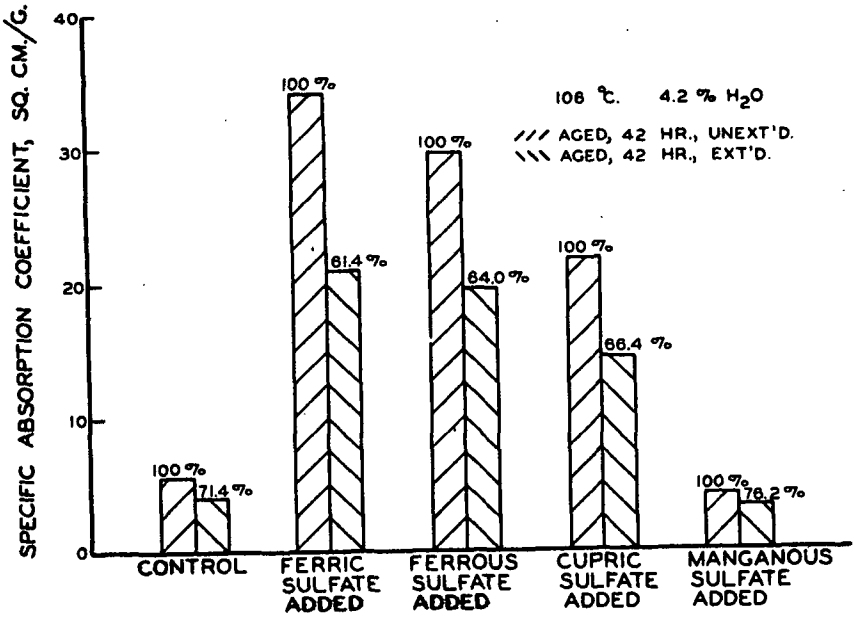


Figure 9. Effect of Acid Extraction on the Specific Absorption Coefficient of Aged Samples

Trial X

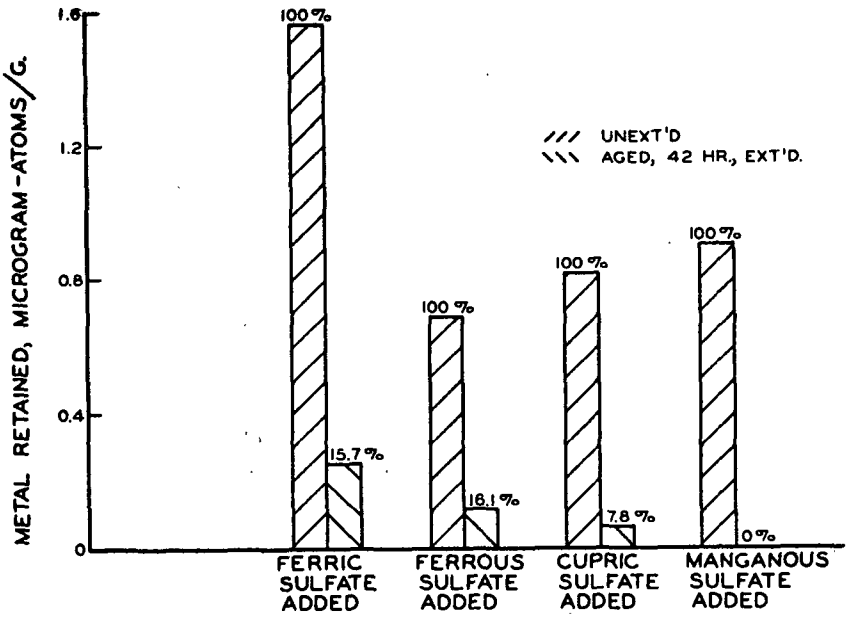


Figure 10. Effect of Acid Extraction on the Metal Content of Pulp

Trial X

TABLE XVII

EFFECT OF ACID EXTRACTION ON THE METAL CONTENT OF PULP

Sample[a]	Metal Retained, microgram-atoms/g. pulp, by Samples Containing the Following Sulfates:				
	Control	Ferric	Ferrous	Cupric	Manganous
Unext'd.	--	1.562	0.689	0.821	0.906
Aged, 42 hrs., ext'd.	--	0.246	0.112	0.064	0.000
difference	--	1.316	0.577	0.757	0.906
difference, %[b]	--	84.3	83.9	92.2	100.0

[a] Measured in Trial X.

[b] % difference = (difference x 100)/unext'd.

aged 42 hours is, of course, impossible on the basis of these results because some of the organic materials were probably extracted and because some of the metals were not extracted. It seems, however, reasonable to conclude that 6/10 to 7/10 of the total color formed during 42 hours of aging was not associated with inorganic materials, and that some, but less than 3/10 to 4/10, was attributable to inorganic materials.

THE EFFECT OF ACETONE PRE-EXTRACTION ON REVERSION

Although the cotton linters used in this investigation were of very high purity, there was the possibility that minor constituents, which had not been removed by prior purification, were responsible for discoloration incurred during accelerated aging. To check this possibility, 30 grams of acid-washed cotton linters pulp were extracted for 6 hours with acetone in a soxhlet extractor. Reflectance disks made from the

extracted linters and unextracted linters were conditioned at 22.9% R.H. and aged 42 hours at 106°C. The initial and terminal absorption coefficients obtained for both pulps are shown in Table XVIII and Figure 11.

Pre-extraction of cotton linters with acetone resulted in slightly less reversion for the control and the sample containing ferric sulfate, and slightly greater reversion for the sample containing manganous sulfate. These differences, however, were small and it appears that any materials removed from cotton linters by acetone extraction were not contributing appreciably to the discoloration incurred during aging.

THE EFFECT OF METALS ON DEPOLYMERIZATION

If the light-absorbing materials formed on cotton linters pulp during accelerated aging are of an organic nature and are not derived from minor constituents, then it appears likely that they are derived from cellulose itself. Both oxidative and hydrolytic degradation of cellulose result in a reduced D.P. If, therefore, either of these reactions are degrading cellulose under the experimental conditions, this fact should be evident by a reduction in the D.P. of the cellulose.

Samples for D.P. determinations were cut from reflectance disks after the absorption coefficient of the disks had been measured. Changes in D.P. occurring during accelerated aging at 4.3% moisture and 105°C. are shown in Table XIX and Figure 12. These data were measured on samples from Trial XIII, and therefore correspond to the optical data shown in Figure 4.

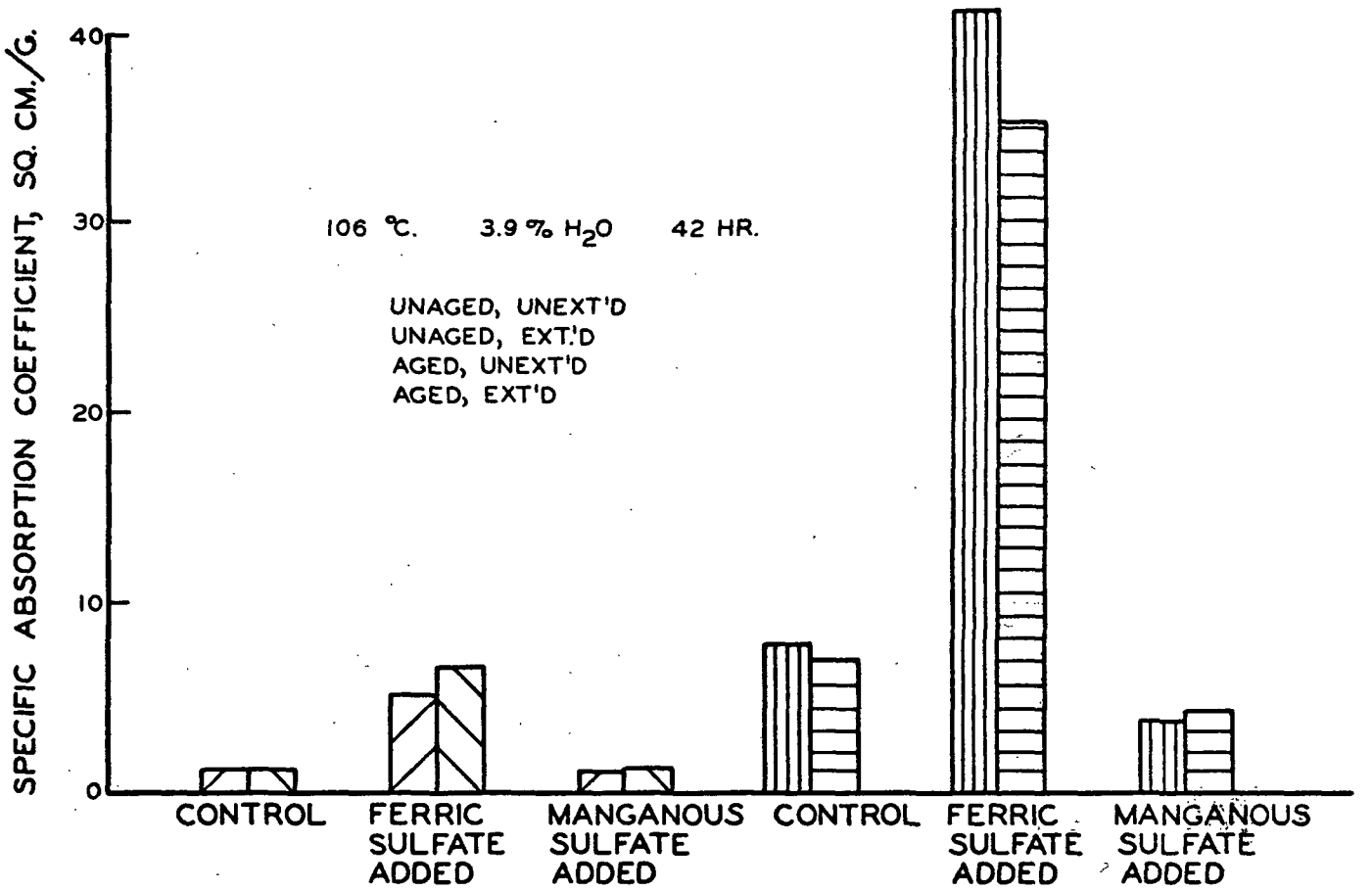


Figure 11. Effect of Acetone Pre-extraction on the Specific Absorption Coefficient

Trial XII

The D.P. of all samples decreased on aging but the magnitude of this decrease was greater in linters containing iron or copper sulfates than it was for the control or the sample containing manganous sulfate.

Within certain limitations, changes in intrinsic fluidity are a more direct measure of chain breakage than changes in intrinsic viscosity or D.P. (41). The data in Table XIX were recalculated and replotted as intrinsic fluidities in Figure 13. These curves show clearly that the rate of chain breakage was accelerated by the presence of iron and copper salts and was slightly retarded by manganese salts. Fluidity curves for the control and samples containing manganese and copper salts were linear

TABLE XVIII

EFFECT OF ACETONE PRE-EXTRACTION ON DISCOLORATION

Sample[a]	Specific Absorption Coefficients, sq. cm./g., of Samples Containing the Following Sulfates:		
	Control	Ferric	Manganous
Unaged, unext'd	1.24	5.07	1.23
Unaged, ext'd	1.28	6.72	1.27
Aged, Unext'd[b]	7.91	41.3	3.82
Aged, ext'd[b]	6.89	35.3	4.31

[a] Measured in Trial XII

[b] Aged at 3.9% moisture and 106°C. for 42 hours.

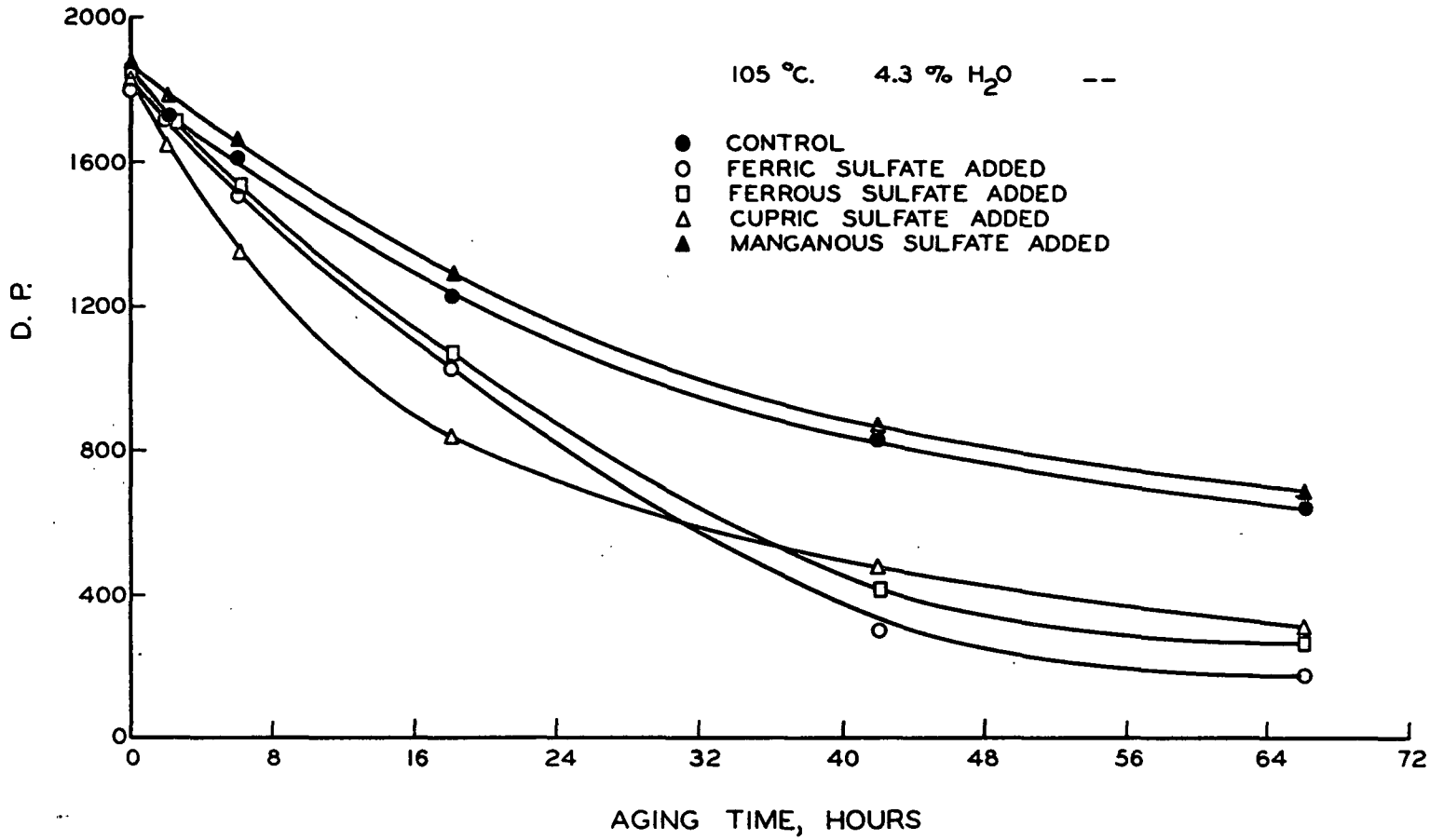


Figure 12. D.P. vs. Aging Time

Trial XIII

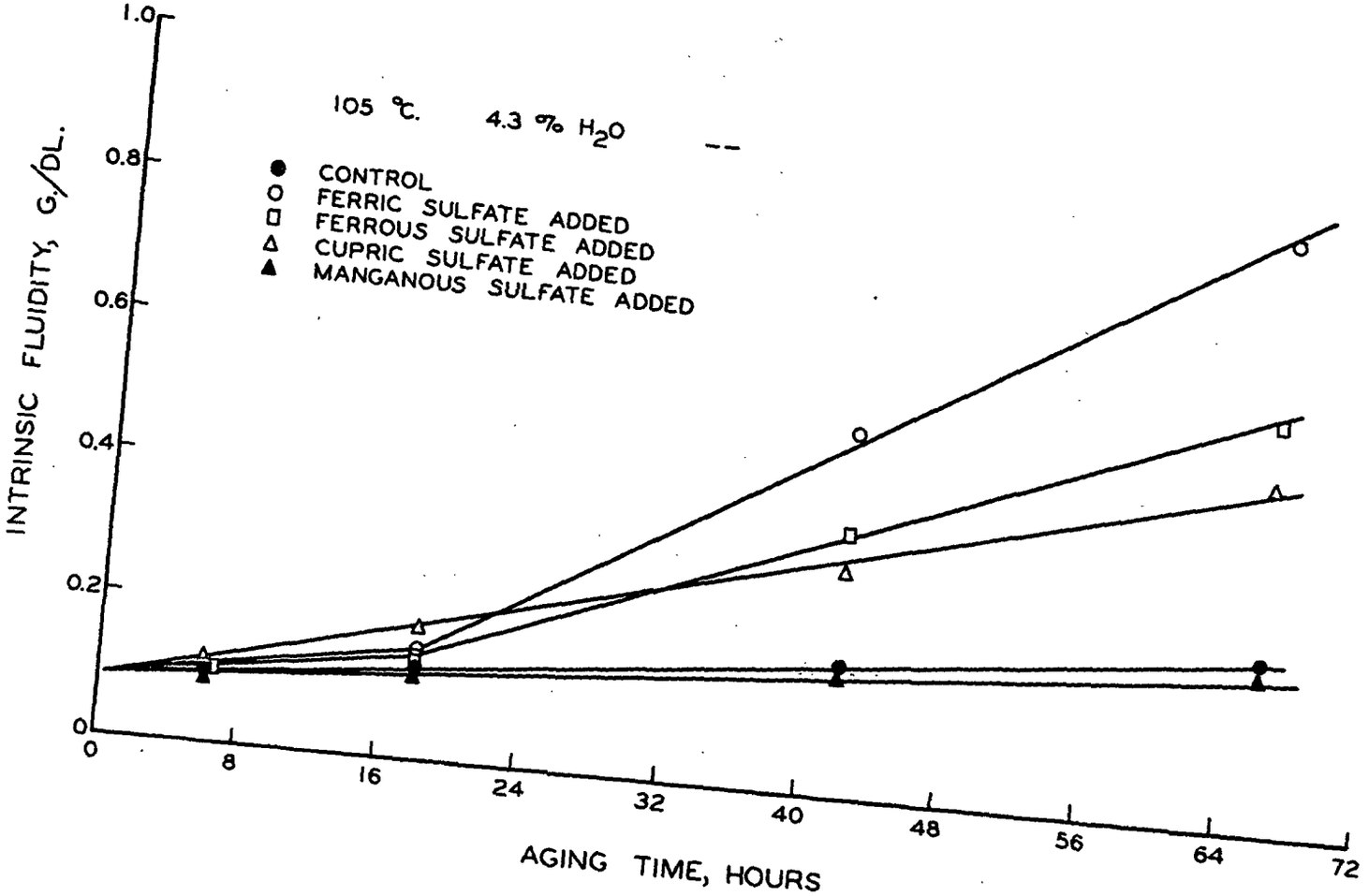


Figure 13. Intrinsic Fluidity vs. Aging Time

Trial XIII

TABLE XIX

EFFECT OF ACCELERATED AGING ON D.P.

Aging Time,[a] hours	D.P. of Samples Containing the Following Sulfates				
	Control	Ferric	Ferrous	Cupric	Manganous
0	1815	1845	1845	1830	1860
2	1740	1725	1725	1650	1785
6	1620	1515	1530	1350	1665
18	1227	1056	1032	839	1289
42	830	297	410	481	874
66	644	183	266	321	692

[a] Measured in Trial XIII; aged at 105°C. and 4.3% moisture.

for the entire aging interval. The fluidities of iron-containing samples, however, increased linearly with time for the first 18 hours of aging and appear to have increased linearly for the 18-66 hour interval though at a different rate than for the first 18 hours.

The linearity of the intrinsic fluidity vs. time plots suggests that chain cleavage was a zero order reaction.

Comparison of Figures 13 and 4 suggests that there is a parallelism between the intrinsic fluidity and specific absorption coefficient of aged linters. Both properties increased with aging. Moreover, the rates of increase for both properties were accelerated by the presence of iron and copper sulfates, and slightly retarded by manganous sulfate.

TABLE XX

EFFECT OF AGING ON INTRINSIC FLUIDITY

Trial No.	Aging Temp.[a] °C.	Moisture Content, %	Intrinsic Fluidities, dl./g., of Samples Containing the Following Sulfates:				
			Control	Ferric	Ferrous	Cupric	Manganous
VI	25	--	0.0730	0.0735	0.0746	0.0780	0.0730
V	100	4.1	0.123	0.185	0.196	0.156	0.116
VII	105	4.3	0.182	0.370	0.370	0.348	0.164
VI	107	0.0	0.0863	0.0902	0.0944	0.0870	0.0827
		4.2	0.219	0.690	0.575	0.481	0.209
		6.9	0.208	0.362	0.290	0.378	0.177
		11.4	0.185	0.272	0.259	0.316	0.159

[a] All samples were aged 42 hours.

The data summarized in Table XX and Figures 14 and 15 show how the intrinsic fluidity varied with moisture content and temperature during aging. Comparison of these graphs with Figures 5 and 6 further suggests that changes in intrinsic fluidity and changes in $\underline{k}$ parallel each other.

The correlation between absorption coefficient and intrinsic fluidity for data from several independent trials is shown in Figure 16. This figure suggests that there is a nearly linear relationship between $\underline{k}$ and the amount of chain breakage incurred by the cotton linters during accelerated aging.

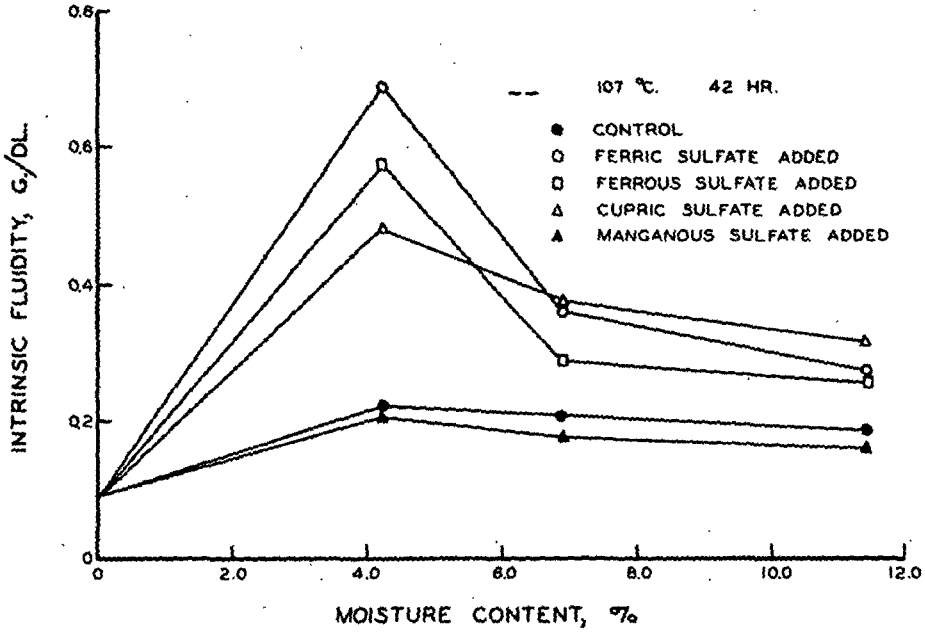


Figure 14. Intrinsic Fluidity vs. Moisture Content

Trial VI

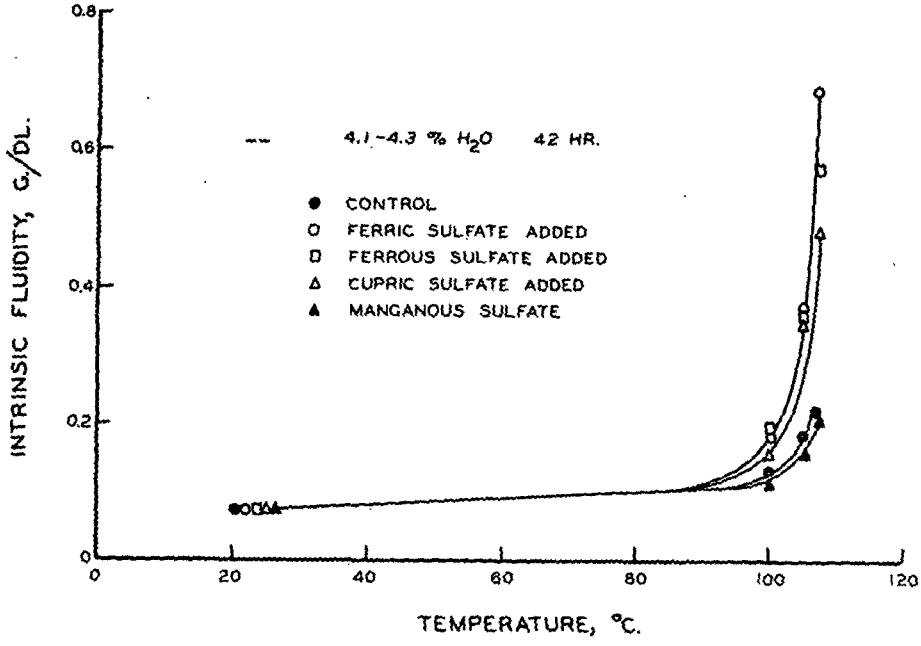


Figure 15. Intrinsic Fluidity vs. Temperature

Trials V-VII

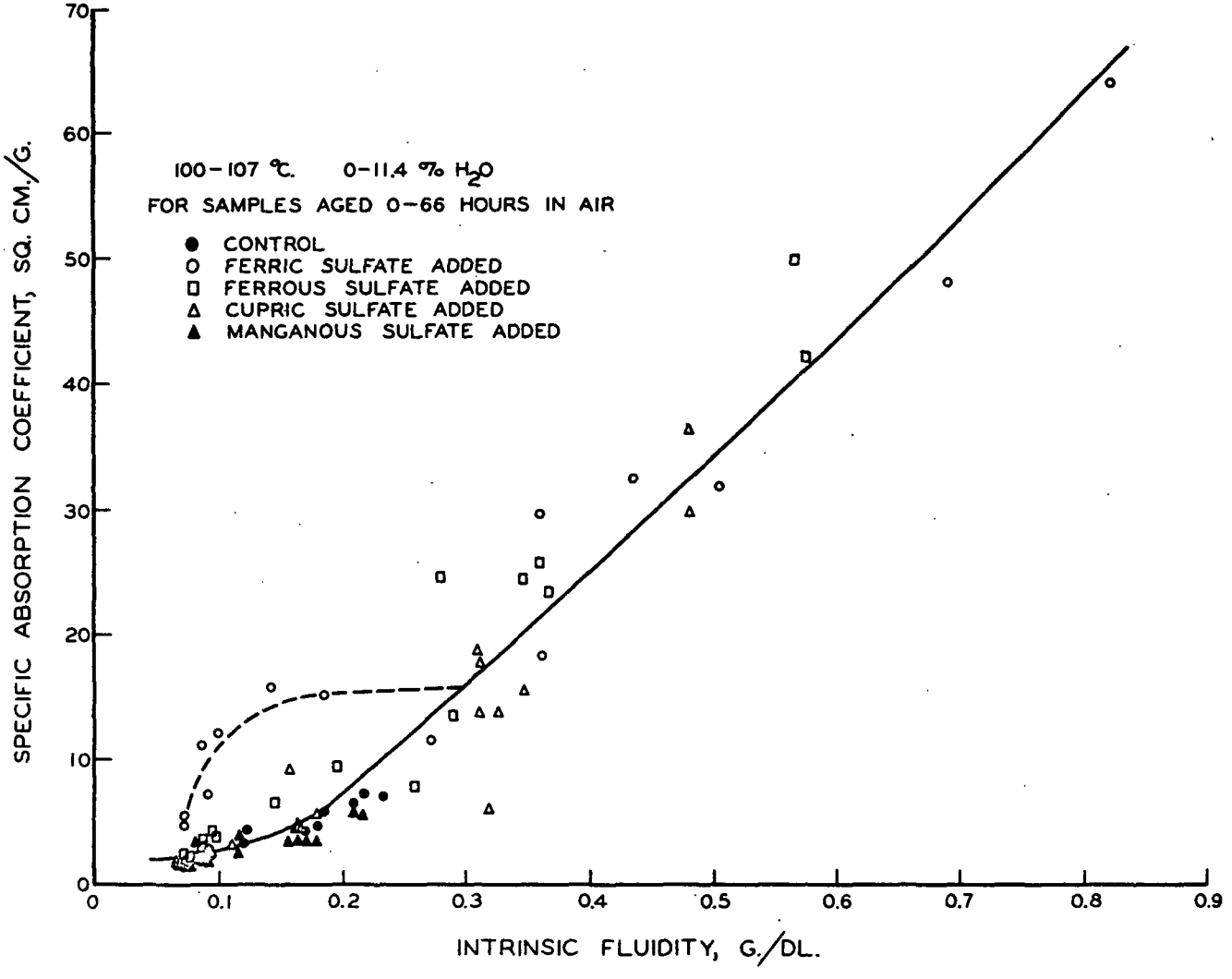


Figure 16. Specific Absorption Coefficient vs. Intrinsic Fluidity

Trials V-VII, IX, XIII

This relationship is not of general value since there undoubtedly are other types of pulps having high fluidities (low D.P.'s) and low absorption coefficients. The significant fact is that large increases in k appear to have occurred only where extensive chain breakage has also occurred.

THE INFLUENCE OF ATMOSPHERIC OXYGEN ON REVERSION

In order to determine the extent to which atmospheric oxygen participated in metal-induced reversion, samples of cotton linters were conditioned in an atmosphere of nitrogen containing less than 0.1% oxygen. The relative humidity of the nitrogen atmosphere was maintained at approximately 23% in order to achieve a moisture content of about 4%. Without removing the samples from the nitrogen atmosphere, they were sealed in aging chambers and aged at 105°C. with other samples conditioned in air at 22.9% R.H. to a moisture content of 4.2%.

The absorption coefficients of both sets of samples after 42 hours of aging are shown in Table XXI and Figure 17. These data indicate that reduction of the oxygen concentration in the aging atmosphere from 21% to less than 0.1% reduced the extent of reversion only 10% for the control and 16-20% for the metal-containing samples.

These results, together with consideration of the nature and concentration of the metal salts added to the linters, suggest that reactions other than oxidation were responsible for the major portion of metal-induced brightness reversion under the specified aging conditions.

TABLE XXI

EFFECT OF ATMOSPHERIC OXYGEN ON DISCOLORATION

Aging Time,[a] hours	Oxygen Content, %[b]	Specific Absorption Coefficients, sq. cm./g. of Samples Containing the Following Sulfates:				
		Control	Ferric	Ferrous	Cupric	Manganous
0	—	1.23	4.86	1.90	1.34	1.26
42	21	4.33	32.4	24.6	18.9	3.46
42	<0.1	4.04	27.6	20.0	16.1	3.02
	Δk_{n2} x 100/Δk air, %	90.6	82.6	80.0	84.0	80.0
	(Δk air-Δk_{n2})100/Δk air, %	9.4	17.4	20.0	16.0	20.0

[a] Measured in Trial IX; aged at 105°C. and 4.2% moisture.

[b] Volume per cent.

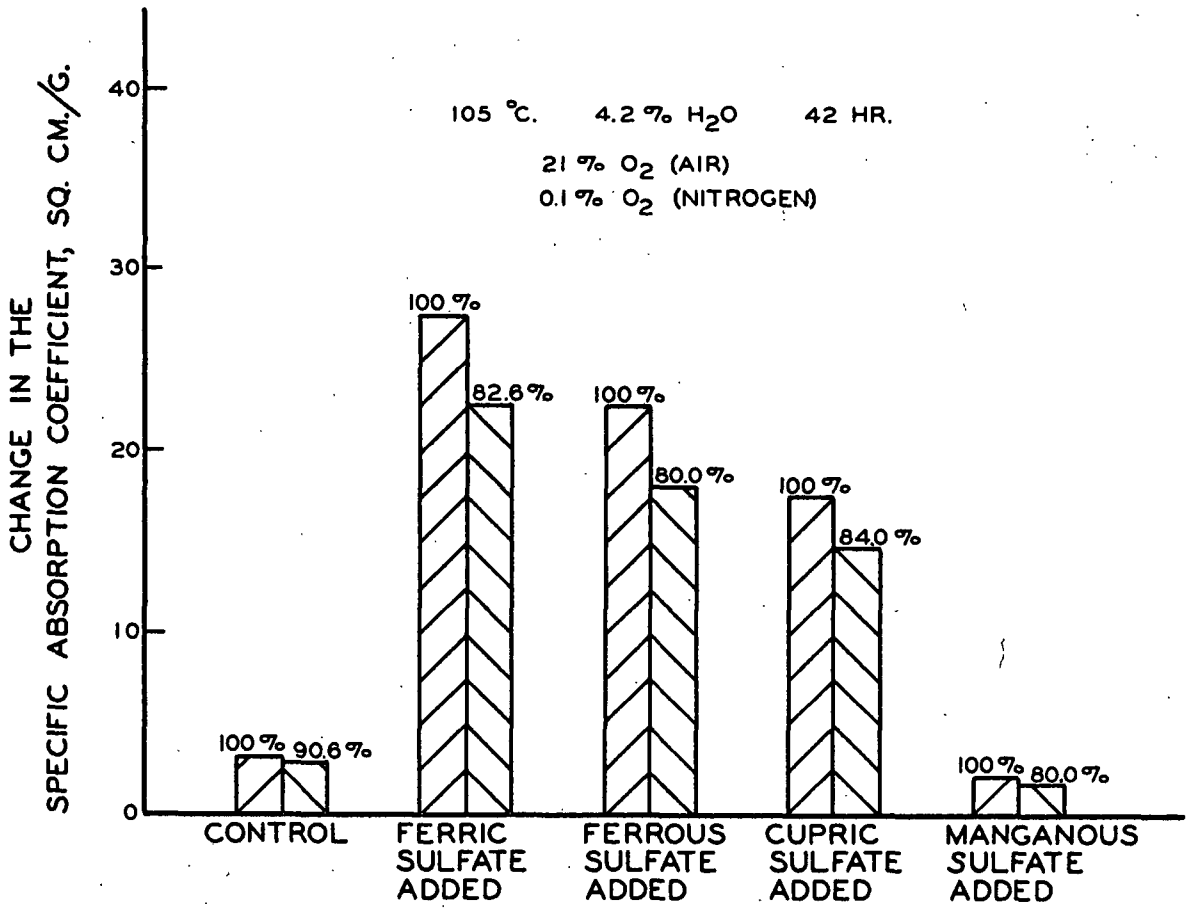


Figure 17. Effect of Atmospheric Oxygen on The Change in The Specific Absorption Coefficient

Trial IX

The D.P.'s of air-aged and nitrogen-aged samples are shown in Table XXII and Figure 18. These same data expressed in terms of intrinsic fluidity are shown in Figure 19. Elimination of atmospheric oxygen reduced the change in D.P. between 26 and 36%, and the change in intrinsic fluidity 44 to 77%. Atmospheric oxygen, it thus appears, had a greater effect on depolymerization than on discoloration.

ULTRAVIOLET AND INFRARED SPECTRA OF COTTON LINTERS

If colored organic materials of a particular type were a cause of metal-induced reversion, then it might be possible that they, or intermediates involved in their formation, could be identified on the cotton fibers. In an effort to make such an identification, samples of cotton linters from Trial III were analyzed spectrophotometrically in the wavelength range of 230 mmu to 15 mu.

ULTRAVIOLET SPECTRA (230 mmu-400mmu)

Ultraviolet reflectance curves were obtained through the courtesy of the Beckman Instrument Company on a Beckman DK-2 Recording Spectrophotometer equipped with a reflectance attachment. The reflectance, R_∞, of thick pads was measured in reference to a magnesium carbonate block in the same manner as with the GERS in the visible region.

Reflectances read from the reflectance curves were converted to k/s ratios using the Kubelka-Munk equation,

$$k/s = (1-R_\infty)^2/2R_\infty$$

TABLE XXII

EFFECT OF ATMOSPHERIC OXYGEN ON D.P.

Aging Time,[a] hours	Oxygen Content, %[b]		D.P. of Samples Containing the Following Sulfates				
			Control	Ferric	Ferrous	Cupric	Manganous
0	—		2055	2055	2055	2055	2055
42	21		897	344	540	480	968
42	<0.1		1193	969	1013	1035	1260
		ΔD.P.$_{n2}$ x 100/ΔD.P. air, %	74.0	63.2	68.4	64.8	73.6
		(ΔD.P. air-ΔD.P.$_{n2}$) x 100/ΔD.P. air, %	26.0	36.8	31.6	35.2	26.4

[a] Measured in Trial IX; aged at 105°C. and 4.2% moisture.

[b] Volume per cent.

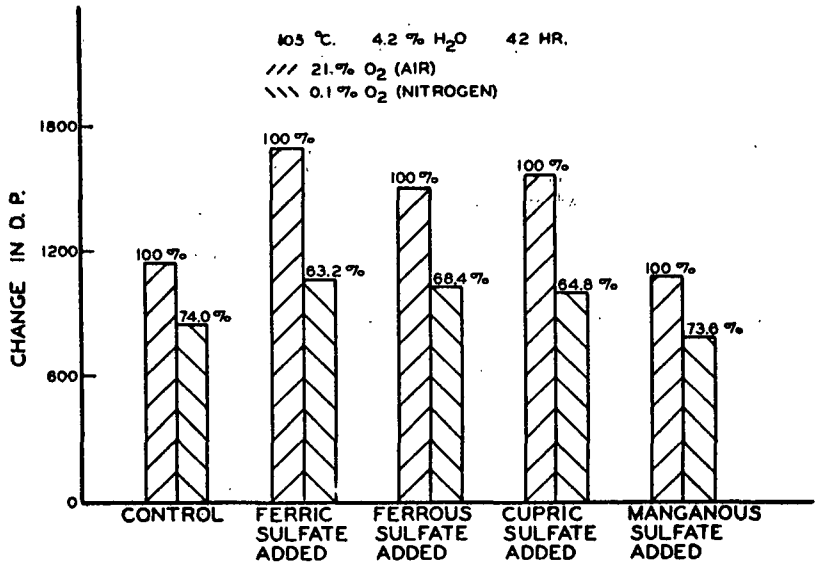


Figure 18. Effect of Atmospheric Oxygen on The Change in D.P.

Trial IX

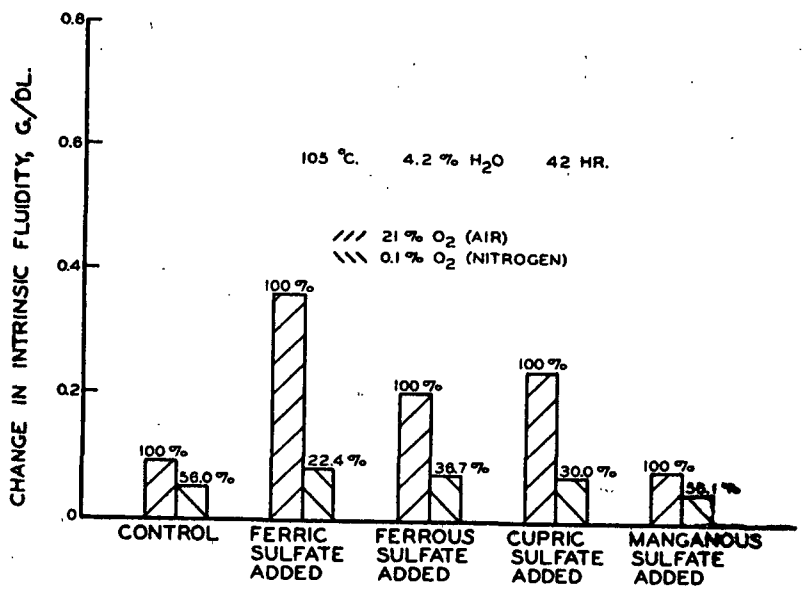


Figure 19. Effect of Atmospheric Oxygen on the Change in Intrinsic Fluidity

Trial IX

For these calculations the reflectance of the magnesium carbonate was taken as being 100%. This was necessary because the correction factors (see APPENDIX p.) required to convert the measured reflectances to absolute values were not available. Since, however, these data were compared internally, the above assumption should not seriously hinder conclusions drawn from them.

Values of k/s for unaged samples of Trial III are shown in Figure 20 and for aged samples in Figure 21. Data for wavelengths between 270 and 280 mmu are not included because reflectances below 280 mmu were determined several weeks later than reflectances above 270 mmu. The two sets of data did not coincide where they overlapped, making the precise location of the k/s curves uncertain. All reflectances below 280 mmu were measured at the same time so that there is no uncertainty as to the occurrence of maxima in k/s vs. wavelength plots for aged samples.

Figures 20 and 21 show that a material absorbing selectively at 250-260 mmu was formed on cotton linters during aging, and that larger amounts of this material were formed in samples containing iron and copper sulfates than in the control or the sample containing manganous sulfate. While the nature of the chromophoric group or material responsible for this absorption cannot be stated with certainty, it should be pointed out that compounds which exhibit this type of absorption spectra (42) and which are derivable from cellulose (42, 43) occur among the furan derivatives. Such derivatives should, therefore, be given consideration as possible origins of the absorption maxima in aged cellulose, and as

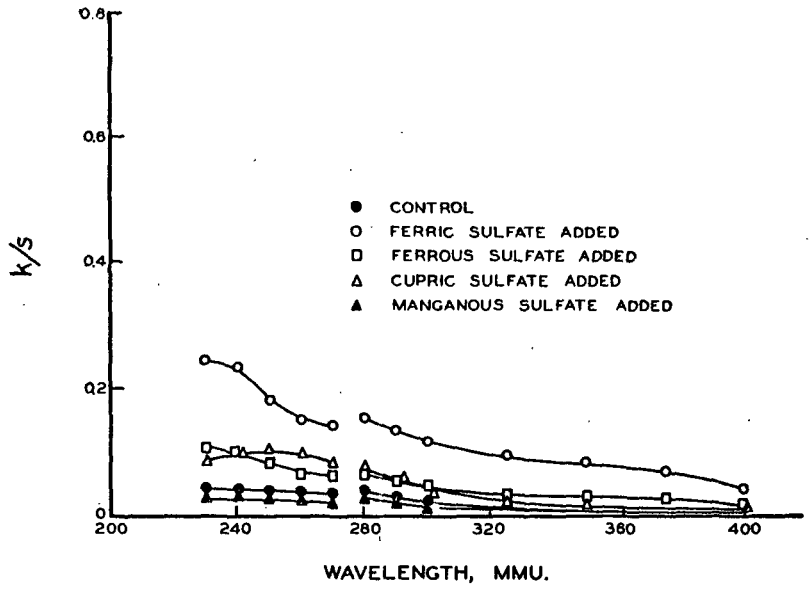


Figure 20. Initial k/s vs. Wavelength

Trial IX

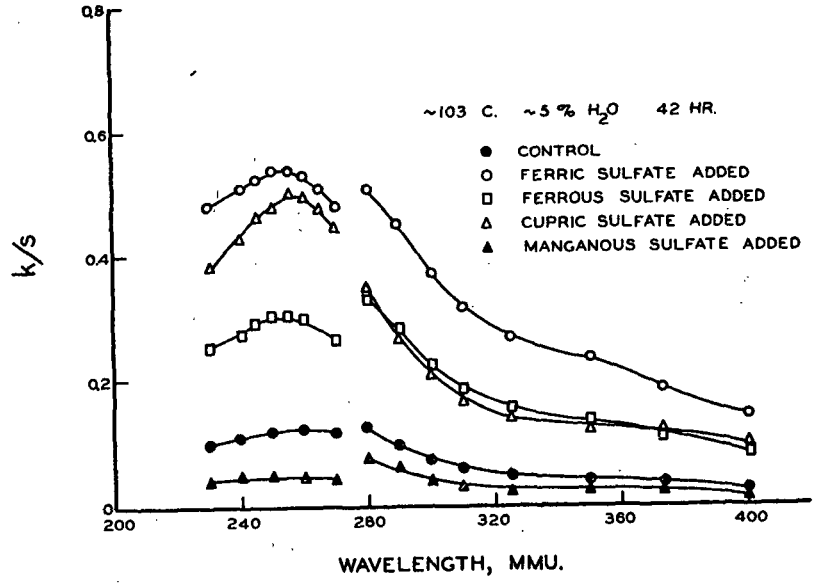


Figure 21. Terminal k/s vs. Wavelength

Trial III

possible intermediates in the reactions causing the discoloration of aged cotton linters.

Similar results have been reported by Lorås and Løschbrandt (44) who found that ultraviolet reflectance curves of aged pulps and alpha fractions of hypochlorite bleached pulps exhibited minima (which correspond to k/s maxima) at 250-260 mmu. They suggested that a dissolution of cellulose to low molecular weight fragments was necessary for this behavior, and mentioned the possibility that oxidation facilitates the formation of furan derivatives which cause the reflectance minima at 250-260 mmu.

VISIBLE (400mmu-700mmu) AND NEAR-INFRARED (700mmu-2.3mu) SPECTRA

Reflectance curves in the visible region were determined on the Beckman DK-2 Recording Spectrophotometer and the GERS. The results from these two instruments were in very close agreement.

Absorption coefficients measured at 457 mmu on the GERS for the samples of Trial III are given in Table XXIII. In this particular trial the sample containing cupric sulfate discolored slightly more than the sample containing ferrous sulfate. This was an atypical result.

The variation of absorption coefficient with wavelength in the visible region for samples from Trial III was similar to that shown for Trial I in Figures 2 and 3.

Reflectance curves in the near-infrared (NIR) were also measured on

the Beckman instrument. Spectra of all samples were identical except near 700 mmu where some curves began to diverge slightly. These differences, however, were very small.

INFRARED (2.0mu-15.0mu) SPECTRA

Transmission spectra in the infrared were determined on a Perkin-Elmer Model 21 Recording Infrared Spectrophotometer. Samples were ground on a Wiley mill, and weighed amounts of the fractions passing through a 40-mesh screen were pressed into pellets with potassium bromide. The per cent transmission of the pellets was then measured as a function of wavelength.

TABLE XXIII

RESULTS OF TRIAL III

Aging Time, hours	Aging Temp., °C.	Moisture Content, %	Specific Absorption Coefficients, sq. cm./g., of Samples Containing the Following Sulfates:				
			Control	Ferric	Ferrous	Cupric	Manganous
0	--	--	1.68	5.59	3.25	1.97	1.76
42	-103	-5	5.40	20.6	16.1	17.5	3.76

The unaged control and the aged copper sulfate-containing sample were analyzed in this way, and no differences were noted in their spectra. Apparently, the materials causing the absorption maxima in the ultraviolet were not present in sufficient amounts to be detected in the infrared where 1.0-0.1 mg. of absorbing material are usually required to produce recognizable spectra.

HYDROXYMETHYLFURFURAL IN AGED COTTON LINTERS

Because in the absence of pentosans the most likely furan derivative which could be formed from cotton linters pulp is hydroxymethylfurfural (HMF), the following experiments were performed to see if this compound could be identified in aged linters.

Four-gram portions of samples from Trial XII (see Table XVIII for optical data) were extracted with 90 ml. of water for about 4 hours at room temperature. The extracts were filtered, diluted with washings to 100 ml., and their ultraviolet transmission spectra determined on a Beckman DK-2 Recording Spectrophotometer using deionized water as a reference. Typical examples of these spectra are shown in Figure 22. Extracts from the aged samples absorbed more strongly than those from unaged samples, and extracts from iron-containing samples absorbed more strongly than those from the control.

The extracts were neutralized with sodium hydroxide to a pH of 7.0-7.5, concentrated under vacuum at 30°C., and spotted on prewashed (with ethyl alcohol) Whatman No. 1 chromatographic paper. Known amounts of HMF were also spotted on the paper chromatogram which was developed for approximately 18 hours with butanol saturated with 2% aqueous ammonia. After the chromatogram was dried and the known HMF spots identified with color reagents or an ultraviolet lamp, those areas of the paper suspected to contain HMF from the extracts were cut out and eluted with ethyl alcohol. The eluates were diluted to 5 ml. and their ultraviolet absorption spectra determined using the alcoholic eluate from an equal

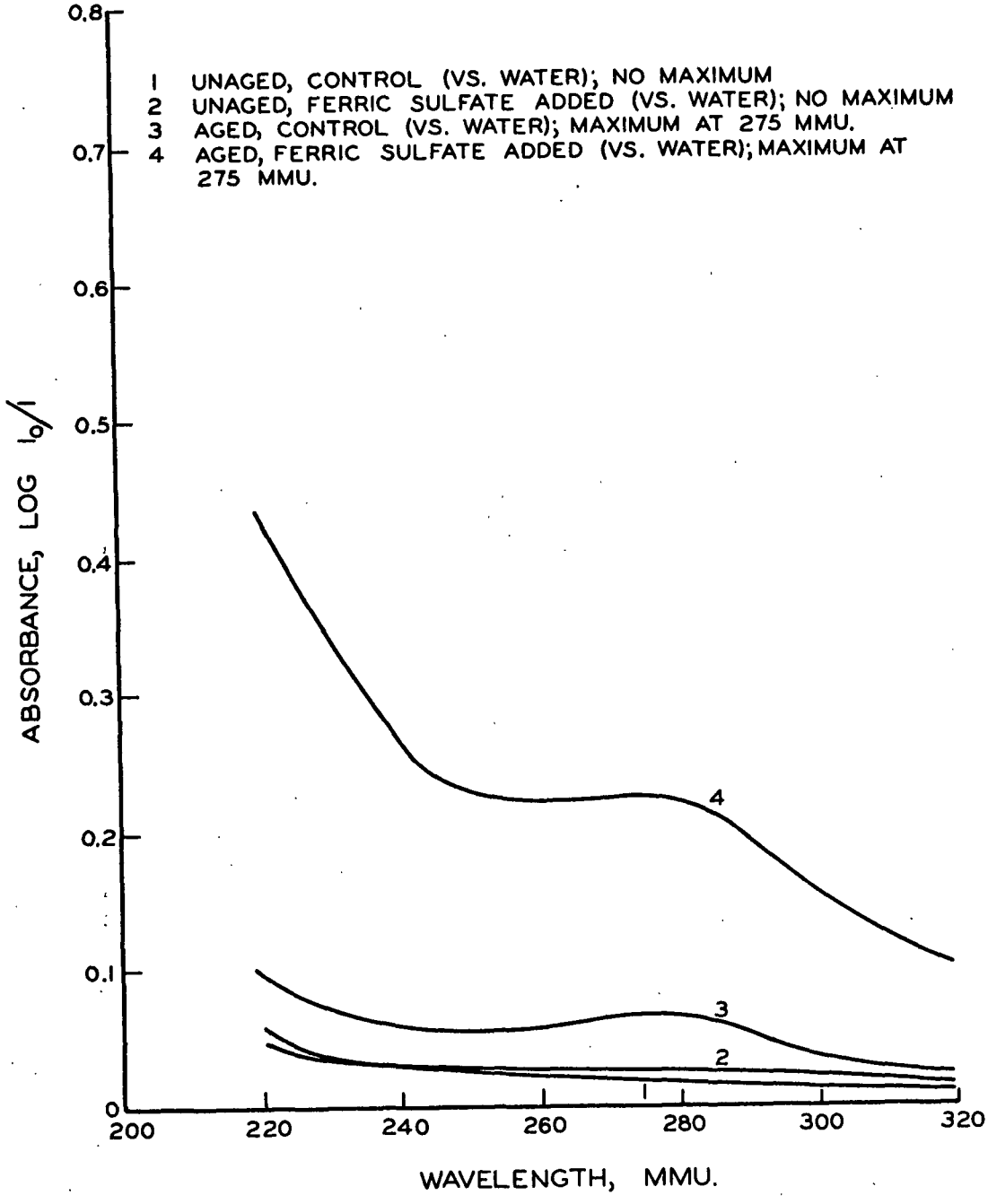


Figure 22. Ultraviolet Absorbance of Aqueous Extracts From Cotton Linters

area of the chromatogram as a reference. These spectra are shown in Figure 23 as curves 1-3. The absorption spectrum of HMF similarly eluted from a developed chromatogram was also measured relative to the alcoholic reference. This is shown as curve 4 in Figure 23.

The absorption spectrum of an aqueous solution containing 5.0 micrograms of HMF (purity 98%) per ml. was determined using deionized water as the reference. Curve 5 in Figure 23 represents this result.

The spectrum of the alcoholic reference was measured relative to ethyl alcohol and is shown as curve 6 in Figure 23. It is apparent that the alcoholic reference absorbs strongly at wavelengths below 240 mmu and therefore little significance should be attached to portions below 240 mmu of spectra, i.e., curves 1-4, measured relative to this reference.

Log absorbance vs. wavelength curves for HMF eluted from the chromatogram and for the extract from the aged sample containing ferric sulfate are shown in Figure 24. In this figure the curves have been shifted on the log absorbance scale to coincide at 281 mmu in order to compensate for the difference in their concentrations. The two curves were quite similar in the wavelength range 240-310 mmu. This suggests that the same material may be responsible for the absorption of both solutions.

Assuming that HMF is actually responsible for the absorption maxima in extracts from aged samples, the concentration of HMF in these extracts may be estimated at 0.5 micrograms per ml. for the aged control (curve 2) and 1.2 micrograms per ml. for the aged ferric sulfate-containing sample (curve 5).

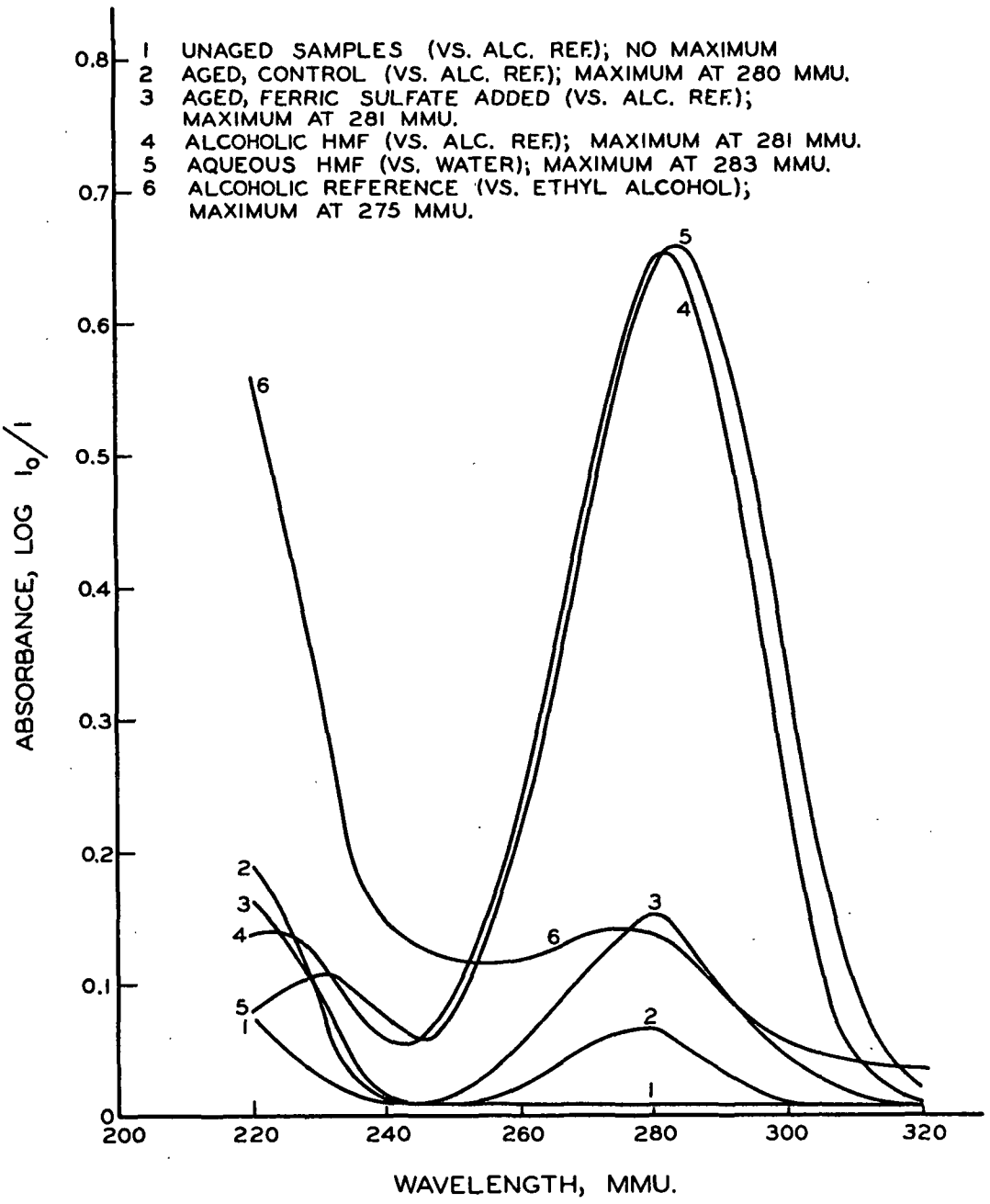


Figure 23. Ultraviolet Absorbance (Differential) of Alcoholic Eluates

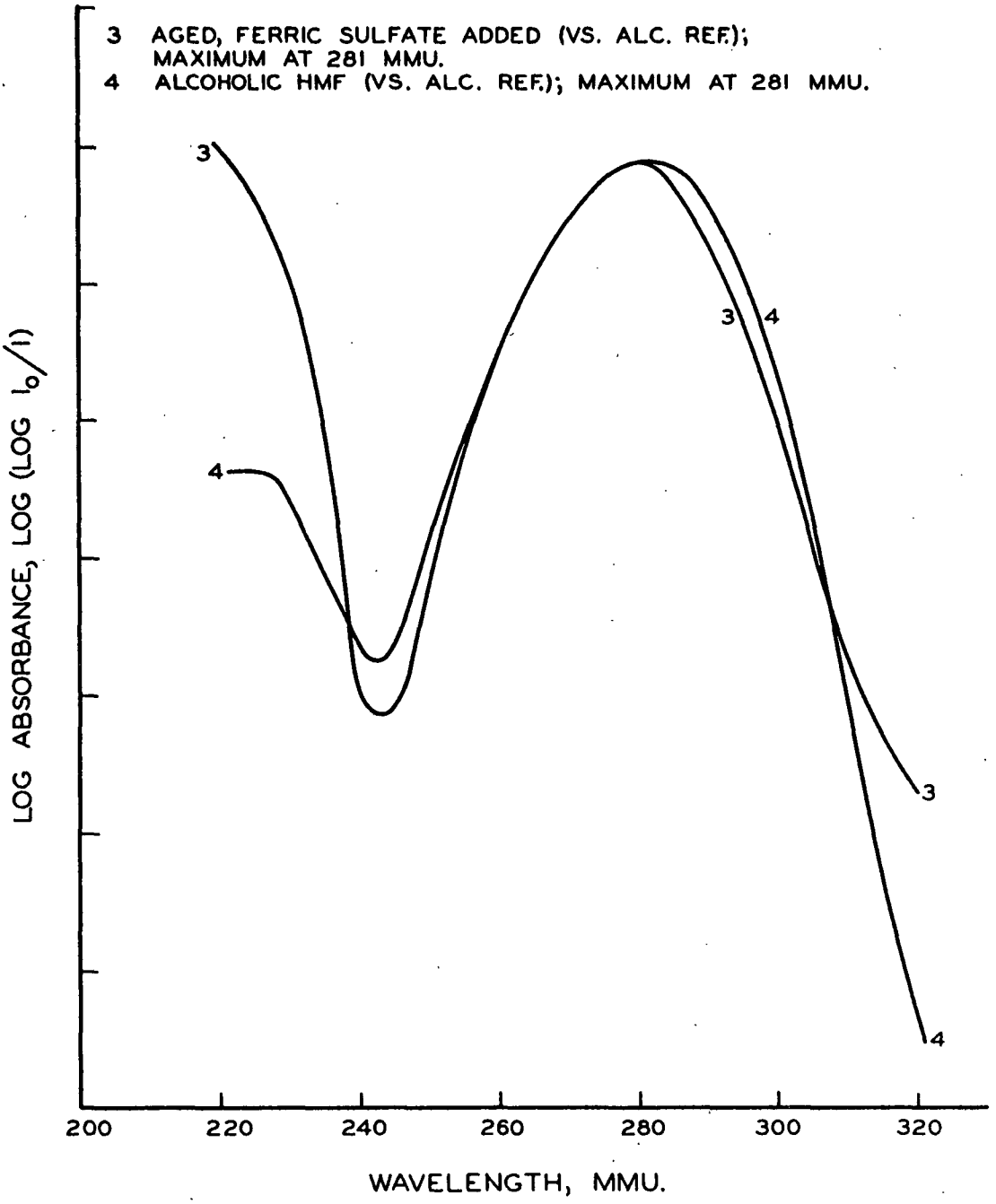


Figure 24. Ultraviolet Absorbance of Alcoholic Eluates

sample (curve 3). The basis for these estimations is the absorbance at 281 mmu of the solution containing 5.0 micrograms of HMF per ml. (curve 5).

Additional details of the chromatographic methods used in this experiment and a description of analytical techniques for identifying HMF via infrared spectral analysis are given in the APPENDIX p. 113.

KINETIC CONSIDERATIONS

On the basis of the foregoing experimental results it is possible to hypothesize that one mechanism by which cotton linters could undergo reversion on aging consists of a hydrolytic degradation of cellulose to low molecular weight products and a subsequent dehydration and perhaps condensation of these products to highly colored materials. If such a mechanism does actually occur, then the observed rate of discoloration should be consistent with the rate of product formation calculated for two consecutive reactions which obey the same rate laws as hydrolysis and dehydration of carbohydrates.

Although a divergence of opinion exists about the actual kinetics involved in the heterogeneous hydrolysis of cellulose, zero order kinetics are generally believed to best describe low levels of degradation (41). Results obtained in this investigation support this belief (see EXPERIMENTAL RESULTS p. 63 and Figure 12 p. 61).

Dehydration of hexose sugars can lead to the formation of HMF but the kinetics of this reaction have not been described. The formation of furfural from xylose, on the other hand, has been studied and is considered

to be a first order reaction (42). Resinification of furfural in dilute, acidic, aqueous media is also believed to be a pseudo-unimolecular reaction (42), i.e., a first order reaction in which more than one molecule is involved (33). If the reactions of glucose and HMF are assumed to be analogous to those of xylose and furfural, then the occurrence of first order reactions in the second step of the proposed mechanism seems quite possible.

Certainly the reactions proposed to follow hydrolysis must occur in several steps and probably involve several intermediates, each of which forms and reacts according to individual kinetic laws. For an over-all reaction consisting of first order reactions, the over-all rate is dependent upon the rate of the slowest reaction in the sequence (45). For this analysis, therefore, it is assumed that a single first order rate equation can descibe the over-all rate of the several reactions making up the second step of the proposed mechanism.

For a reaction,

$$A \xrightarrow{r_1} B \xrightarrow{r_2} C$$

in which reactant A forms product B according to zero order kinetics with a rate constant of r_1 [moles/(liter-hr.)], and B reacts further to form product C according to first order kinetics with a rate constant of r_2 [1/hr.], it may be said that

$$dy/dt = r_1 - r_2 y, \text{ and}$$

$$dz/dt = r_2 y.$$

In these equations y is the concentration (moles/liter) of B and z the concentration (moles/liter) of C at time t. Integrating and solving these equations (see APPENDIX p. 138) for z as a function of time yields the following expression:

$$z = r_1 (t + e^{-r_2 t}/r_2 - 1/r_2).$$

The variation of z as a function of time for assumed values of r_1 and r_2 is shown in Figure 25. Also shown in this figure are the observed rates of reversion for cotton linters with and without added metal sulfates.

From Figure 25 it appears that the rates of metal-induced reversion in cotton linters pulp during the aging interval of 2-66 hours can be described by rate curves calculated for two consecutive reactions, the first of which is a zero order reaction and the second of which is a slower first order reaction. This result suggests that a hydrolysis-dehydration-condensation mechanism of reversion is not inconsistent with kinetic considerations.

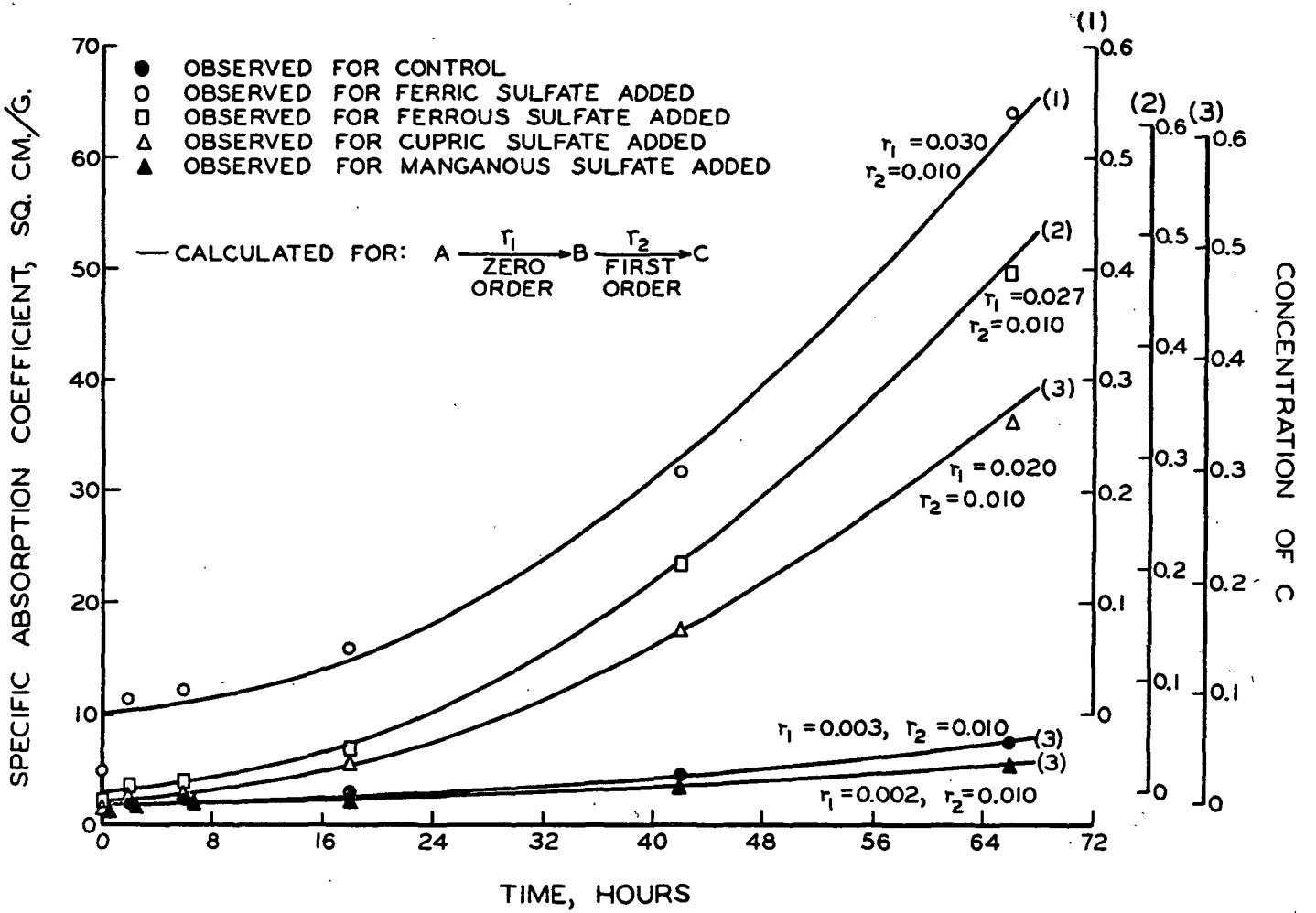


Figure 25. Specific Absorption Coefficient vs. Aging Time and Concentration of C vs. Time

Trial XIII

SUMMARY

Metal salts were added to slurries of purified cotton linters pulp and the specific absorption coefficient, $\underline{k}$, of reflectance pads made from the slurries was measured. Sulfates of iron, copper, and manganese were used in all trials except two, in which the chlorides and acetates of these metals were used. Sulfates of magnesium, lanthanum, cadmium, and aluminum were included in two trials.

The reflectance pads were conditioned in an atmosphere of known relative humidity, e.g., 23, 50, 76, 87% R.H., sealed in aging chambers, and heated in an oven at a controlled temperature in the range of 100-107°C. After the desired aging interval had elapsed the pads were removed from the aging chambers and their specific absorption coefficients re-determined. These terminal absorption coefficients were used directly as a measure of the extent of reversion.

The observations which were made are summarized as follows:

1. Measurements of the specific absorption coefficients, $\underline{k}$, were reproducible to within $\pm$ 5% at the 95% confidence level.
2. The maximum coefficient of variation for initial absorption coefficients, $\underline{k}_0$, or terminal absorption coefficients, $\underline{k}_{42}$, measured after similar treatments in different trials was $\pm$ 17%.
3. Values of $\underline{k}$ for all samples of cotton linters became larger, but showed no evidence of having a maximum value, when the wavelength at which they were measured was decreased from 700 to 400 mmu.

4. The addition of 1 p.p.m. of metal salts to pulp slurries increased the k_o of reflectance pads made from the slurries. For example, the average value of k_o for the control was 1.30 sq. cm./g., while for the sample containing ferric sulfate it was 4.70, for ferrous sulfate 2.13, cupric sulfate 1.63, and manganous sulfate 1.27 sq. cm./g. (Trial XIII).
5. Absorption coefficients of all samples, especially those containing ferric or ferrous sulfate, increased rapidly during the first two hours of accelerated aging.
6. After the first two hours of aging, k appeared to increase exponentially with respect to aging time.
7. After 42 hours of aging at 105°C. and 4.3% moisture, typical values of k_{42} were: 4.76 sq. cm./g. for the control, 31.6 for the sample containing ferric sulfate, 23.5 for ferrous sulfate, 17.7 for cupric sulfate, and 3.54 sq. cm./g. for manganous sulfate (Trial XIII).
8. The relative effect of metal sulfates in accelerating reversion was the same for all aging conditions and all trials (except Trials I and III where cupric sulfate caused slightly greater reversion than ferrous sulfate).
9. The order in which the metal sulfates promoted reversion was: $Fe^{+++} > Fe^{++} > Cu^{++} > Al^{+++} >$ control $> Cd^{++} > La^{+++} > Mg^{++} > Mn^{++}$.
10. In accordance with published data (35, 36) the order in which the metal sulfates hydrolyzed in solution was found (see Tables V and VI) to be:

$$Fe^{+++} > Al^{+++} > Fe^{++} > Cu^{++} > Cd^{++} > La^{+++} > Mn^{++} > Mg^{++}.$$

11. Iron and copper sulfates had a maximum accelerating effect on reversion in cotton linters at a moisture content which, for the points actually tested, was approximately 4%. Samples, for example, which contained cupric sulfate and had been aged 42 hours at 107°C. had absorption coefficients of 3.2 sq. cm./g. after aging under dry conditions, 29.8 sq. cm./g. after aging at 4.2% moisture, 13.6 sq. cm./g. at 6.9% moisture, and 5.9 sq. cm./g. at 11.4% moisture.

12. The extents of reversion for the control and for the sample containing manganous sulfate were not so greatly affected by the moisture content during aging as the extents of reversion for the samples containing iron or copper sulfates.

13. Metal-induced reversion in cotton linters was very sensitive to small changes in aging temperature in the range 100-107°C; a change of approximately 5°C. doubled the extent of reversion for iron- and copper-containing samples.

14. For the control and the sample containing manganous sulfate the extent of reversion appeared to double for a 10°C. rise (extrapolated).

15. The chlorides and acetates of copper, manganese, and ferrous iron had the same effects on $\underline{k}_0$ and $\underline{k}_{42}$ as the respective sulfates.

16. The chloride and acetate of ferric iron caused larger increases in $\underline{k}_0$ and $\underline{k}_{42}$ than the sulfate, presumably because of the darker color or greater retention of these salt solutions.

17. The quantity of each metal sorbed was remarkably constant for

slurry concentrations of 0.5 to 5.0 p.p.m.; depending on the metal, the amounts sorbed ranged from 0.7 to 1.5 microgram-atoms of metal per gram of pulp.

18. Reflectance pads prepared from slurries which contained no added salts but which had been acidified with sulfuric acid to a pH of 4.0, did not discolor to any greater extent than pads prepared from unacidified slurries having a pH of 5.5 to 6.0.

19. The terminal absorption coefficient, $\underline{k}_{42}$, of a sample (free of added salts), to which 2.3 micromoles of sulfuric acid per gram of linters had been added, was 10.7 sq. cm./g. after aging at 105°C. and 4.0% moisture. For a control, $\underline{k}_{42}$ was 3.95 sq. cm./g., and for a sample containing ferric sulfate it was 30.2 sq. cm./g.

20. The amount of sulfate sorbed by cotton linters pulp when it was treated with ferric sulfate appeared to be equivalent to less than half of the sorbed iron regarded as ferric sulfate (1.5 microgram-atoms of iron or 2.3 micromoles of sulfate).

21. Extraction of unaged, metal-containing reflectance pads with a dilute mixture of hydrochloric and hydrofluoric acids restored their absorption coefficients, $\underline{k}_{o}$, to that of the control.

22. Similar acid extraction of metal-containing samples which had been aged two hours restored their absorption coefficients, $\underline{k}_{2}$ to that of the control.

23. Acid extraction of metal-containing samples which had been aged 42 hours reduced their absorption coefficients, $\underline{k}_{42}$, only 24 to 38%, but removed 84 to 100% of the added metals.

24. Further purification of cotton linters by extraction with acetone before preparation of reflectance pads did not have a significant effect on the extent of reversion for either the control or the samples containing ferric or manganous sulfates.

25. During accelerated aging the intrinsic fluidities, [Ⓕ] of the control and of the samples containing cupric and manganous sulfates increased linearly with time.

26. Intrinsic fluidities of samples containing iron sulfates appeared to increase linearly with aging time, but at a different rate during the first 18 hours than during the next 48 hours.

27. The order in which the metal sulfates promoted depolymerization (as indicated by the intrinsic fluidity measured after 42 hours of aging) was the same as the order in which they accelerated reversion, namely:

$$Fe^{+++} > Fe^{++} > Cu^{++} > \text{control} > Mn^{++}.$$

28. Iron and copper sulfates had a maximum accelerating effect on depolymerization at a moisture content which, for the points actually tested, was approximately 4%. For example, samples which contained cupric sulfate and had been aged 42 hours at 107°C. had intrinsic fluidities of 0.087 g./dl. after aging under dry conditions, 0.481 g./dl. after aging at 4.2% moisture, 0.378 g./dl. at 6.9% moisture and 0.316 g./dl. at 11.4% moisture.

29. Depolymerization in the control and in the sample containing manganous sulfate was less affected by moisture during aging than samples containing iron or copper sulfates.

30. Metal-induced depolymerization of cotton linters was sensitive to small differences in aging temperatures in the range 100-107°C.; a change of approximately 5°C. doubled the extent of depolymerization for samples containing iron or copper sulfates.

31. For the control and the sample containing manganous sulfate, depolymerization was about one half as sensitive to temperature changes as samples containing iron or copper sulfates.

32. In all trials an increase in k was accompanied by an increase in intrinsic fluidity.

33. Reduction of the free oxygen content of the aging environment from 21% (air) to less than 0.1% (nitrogen) reduced the extent of reversion only 10-20%, and depolymerization 26-38% in terms of D.P. or 44-77% in terms of intrinsic fluidity.

34. Within the ultraviolet range of 230-400 mmu., the absorption spectra (k/s *vs.* wavelength) of all aged samples exhibited maxima between 250 and 260 mmu. The height of these maxima was greater for samples aged in the presence of iron or copper sulfates than for the control or the sample containing manganous sulfate (see Figure 21).

35. The ultraviolet absorption spectra of unaged samples did not show maxima in this region.

36. Reflectance spectra (R_∞ *vs.* wavelength) in the near-infrared, and transmission spectra in the infrared were indistinguishable for all samples whether aged or unaged.

37. Ultraviolet absorption spectra of aqueous extracts from aged

samples had maxima at approximately 275 mmu. Similar extracts from unaged samples had no such absorption maxima.

38. From the aqueous extracts of aged samples a small amount of material was chromatographically separated which, within the ultraviolet range of 220-320 mmu, had an absorbance spectrum similar to that of hydroxymethylfurfural between 240 and 310 mmu. (see Figure 24).

39. The rate of reversion after the first two hours of aging can be described by a rate curve calculated for two consecutive reactions, the first being a zero order reaction and the second being a slower, first order reaction.

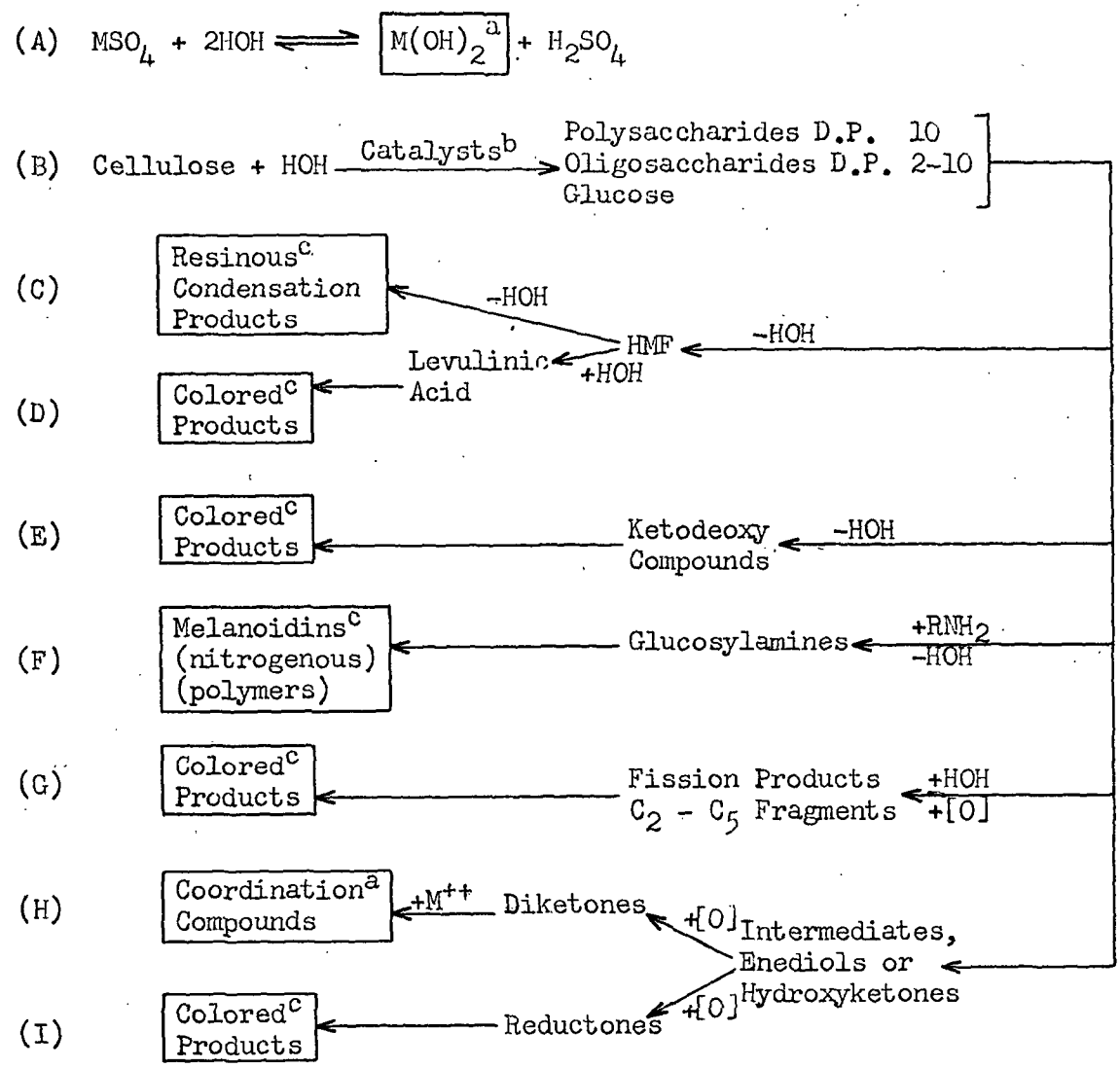
INTERPRETATION OF RESULTS

Although discoloration in materials as chemically and physically complex as papermaking pulps is undoubtedly the result of many different reactions, the accumulated data suggest that, in the case of metal-induced reversion in purified cotton linters, color was formed as the result of the following sequence of reactions:

1. Sorption of metal salts. Cotton linters, suspended in a solution containing 1 p.p.m. of a metal salt, sorb and retain a portion of the salt during handsheet formation. At this low salt concentration, a salt like ferric sulfate will hydrolyze (reaction A in Figure 26), and it is probable that basic hydroxides as well as unhydrolyzed salt are sorbed. This concept is supported by the results of sulfate analyses which suggest that less than half of the iron retained by samples treated with ferric sulfate was sorbed as the unhydrolyzed salt.

   A consequence of this behavior is that handsheets containing ferric sulfate have a larger initial absorption coefficient, k_o, relative to the control, than handsheets containing other metals which have a smaller tendency to hydrolyze or which form less intensely colored hydroxides than ferric hydroxide.

2. Hydrolysis of sorbed metal salts. Raising the temperature of a salt solution, in most cases, causes the hydrolysis constant of the salt to become larger. Therefore, heating handsheets that contain metal salts and moisture might be expected to cause



[a] Source of inorganic color.

[b] Catalysts may be MSO_4, $M(OH)_2$, or H_2SO_4.

[c] Source of organic color.

Figure 26. Some Possible Pathways for Heat-Accelerated, Metal-Induced Brightness Reversion

the sorbed salts to hydrolyze further. This type of reaction, resulting in the formation of additional hydroxide, could account for the increment in $\underline{k}$ formed during the first two hours of aging. This interpretation is supported by the fact that the color formed during this period is readily removed by treatment with dilute acid.

3. Depolymerization of linters. A second phase of reversion is initiated when the linters undergo depolymerization, a reaction which is accelerated by the presence of iron and copper sulfates. Depolymerization may be symptomatic of oxidative, pyrolytic, or hydrolytic degradation. In this investigation, aging was conducted below pyrolytic temperatures, and the only oxidant (atmospheric oxygen) present in sufficient quantities to degrade the linters was removed without greatly reducing the extent of reversion. These facts suggest that the attack was largely hydrolytic in nature.

For hydrolysis of cellulose some water must be present during aging. But if too much moisture is present, the small amounts of inorganic catalysts which promote depolymerization will become too dilute for optimum effect. This concept could account for the maximum which the terminal absorption coefficient, $\underline{k}_{42}$, exhibits at approximately 4.0% moisture.

4. Decomposition of hydrolysis products. Hydrolysis of cellulose (reaction B in Figure 26) may proceed locally to such an extent as to produce low molecular weight fragments and eventually

glucose. But neither the intermediates nor the glucose are colored substances. Hence, it is postulated that glucose, and perhaps other small fragments, undergo further reactions which eventually produce colored substances.

Several pathways can be visualized by which glucose may react under the conditions of aging to yield colored products. Some examples are shown as reactions C through I in Figure 26. Although little can be said about the relative importance of the pathways, the spectrographic indication of hydroxymethylfurfural can be used as an argument that reactions C and D in Figure 26 participate in reversion.

CONCLUSIONS

The data and other information presented in this report warrant the following conclusions:

1. Traces (approximately one microgram-atom of metal per gram of pulp) of certain added metal salts affect the initial absorption coefficient, k_0, of handsheets prepared from purified cotton linters. Increases in k_0 are due almost entirely to the retention of inorganic compounds and occur only if the salt or its hydrolysis products are colored substances.
2. During heat-accelerated aging in sealed chambers at temperatures between 100 and 107°C., the order in which sulfate salts affect the terminal absorption coefficient, k_{42}, is:
   $Fe^{+++} > Fe^{++} > Cu^{++} > Al^{+++} > control > Cd^{++} > La^{++} > Mg^{++} > Mn^{++}$.
   This order, except for the positions of aluminum and magnesium, is consistent with the order of cationic acidity as measured by the pH at which precipitation of the metal hydroxides begins.
3. Although the more pronounced effect of the salts, as measured by k_{42}, is to accelerate reversion, at least in the case of manganese there is significant inhibition of reversion.
4. Metal-induced reversion in cotton linters pulp is dependent on the amount of moisture present during accelerated aging. The terminal absorption coefficient, k_{42}, exhibits a maximum, which, for the points actually tested occurs at about 4% moisture. This effect is most pronounced with iron and copper salts.
5. Metal-induced reversion proceeds in two distinct phases. The

first phase is complete after two hours of accelerated aging, and is due largely to the formation of inorganic reaction products. The second phase, on the other hand, shows no signs of reaching completion even after 66 hours of accelerated aging, and is due largely to the formation of organic reaction products.

6. In its second phase, metal-induced reversion, as measured by the specific absorption coefficient, $\underline{k}$, is in general paralleled by hydrolytic depolymerization as measured by the intrinsic fluidity. Since hydrolysis of cellulose, even to glucose, results only in colorless fragments, the latter must undergo further reactions before the observed increases in $\underline{k}$ can occur. The probable presence of hydroxymethylfurfural may be a clue to the nature of the reactions leading from glucose, etc., to the organic pigments.

7. Kinetically, the sequence of reactions comprising this second phase of metal-induced reversion may be described by an equation calculated for two consecutive reactions, of which the first is a zero order reaction, applicable to the hydrolysis of cellulose, and the second a slower first order reaction, applicable to the dehydration and condensation of the hydrolysis products.

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APPENDIX I

REFLECTANCE CORRECTIONS

All reflectances used in the Kubelka-Munk theory are absolute values. Therefore, reflectances measured on the GERS in reference to magnesium carbonate were corrected to the absolute scale of reflectance. Two corrections were applied. The first made allowance for the individual pecularities of the magnesium carbonate block and converted the measured reflectance to the apparent scale of reflectance for which magnesium oxide is taken as 100%. The second correction converted the reflectance on the apparent scale to the absolute scale.

Let $\underline{R}_m$ represent the measured reflectance, $\underline{R}_{ap}$ the apparent reflectance, $\underline{R}_{ab}$ the absolute reflectance, and $\underline{f}_m$, $\underline{f}_{ap}$, and $\underline{f}_{ab}$ correction factors. Then

$$(\underline{R}_m)(\underline{f}_m) = \underline{R}_{ap}$$

$$\text{and } (\underline{R}_{ap})(\underline{f}_{ap}) = \underline{R}_{ab}$$

$$\text{or } (\underline{R}_m)(\underline{f}_m)(\underline{f}_{ap}) = \underline{R}_m(\underline{f}_{ab}) = \underline{R}_{ab}.$$

Values of the above correction factors are tabulated below in Table XXIV (46).

TABLE XXIV

REFLECTANCE CORRECTION FACTORS

Correction Factor	Wavelength, mmu								
	401	444	457	496	542	579	609	631	656
$\underline{f}_m$	.982	.985	.990	.992	.996	1.000	.999	.998	.999
$\underline{f}_{ap}$	.972	.976	.977	.979	.985	.986	.989	.990	.990
$\underline{f}_{ab}$	.955	.961	.967	.971	.981	.986	.988	.988	.989

APPENDIX II

MOISTURE CALCULATIONS

Let:
t_1 = initial temperature, °C. (23.3)
t_2 = terminal temperature, °C. (100)
p_1 = initial pressure, mm. Hg (760)
p_2 = terminal pressure, mm. Hg
m_1 = initial moisture content, g.
m_2 = terminal moisture content, g.
v = volume of aging chamber, cc.
s = weight of O.D. cellulose, g.
d = density of water at t_1, g./cc. (1.00)
ρ = density of cellulose, g./cc. (1.55)

For initial conditions the volume of dry cellulose is s/ρ and the volume of liquid water is m_1/d. Hence, the volume available for vapor and air is $v-(m_1/d + s/\rho)$. Since the partial pressure of water vapor at 23.3°C. and 50% relative humidity (the initial conditions of the air) is 10.74 mm. Hg, the volume of saturated water vapor is

$$[v-(m_1/d + s/\rho)] (10.74/760),$$

and the volume of dry air is

$$[v-(m_1/d + s/\rho)] [(760-10.74)/760].$$

For terminal conditions the volume of dry cellulose is s/ρ, and the volume of dry air is

$$(p_1/p_2) [v-(m_1/d + s/\rho)] (749.3/760) (373/296).$$

The volume of water vapor which was initially present is

$$(p_1/p_2) [v-(m_1/d + s/\rho)] (10.7/760) (373/296).$$

Hence, the total volume, $\underline{v}_{\underline{x}}$, available for newly formed water vapor and liquid water may be written

$$\underline{v}-\left\{\underline{s}/\rho + (\underline{p}_1/\underline{p}_2)[\underline{v}-(\underline{m}_1/\underline{d} + \underline{s}/\rho)]1.242 + (\underline{p}_1/\underline{p}_2)[\underline{v}-(\underline{m}_1/\underline{d} + \underline{s}/\rho)]0.0178\right\}.$$

The specific volume of vapor at 100°C. is equal to $(\underline{p}_1/\underline{p}_2)1674$ cc./g., and the specific volume of water at 100°C. is 1.043 cc./g. If $\underline{x}$ equals $\underline{m}_2$, the weight of liquid water, and $\underline{y}$ equals the weight of newly formed vapor then

$$1.043\underline{x} + (\underline{p}_1/\underline{p}_2)1674\underline{y} = \underline{v}_{\underline{x}},$$

and

$$\underline{x} + \underline{y} = \underline{m}_1.$$

Solving these two equations simultaneously for $\underline{x}$ the following expression is obtained:

$$\underline{x} = \underline{m}_2 = \frac{(\underline{p}_1/\underline{p}_2)1674\underline{m}_1 - \underline{v}_{\underline{x}}}{(\underline{p}_1/\underline{p}_2)1674 - 1.043} \qquad (1)$$

By substituting the expression for $\underline{v}_{\underline{x}}$ and simplifying, $\underline{m}_2$ can be determined from measured data.

In a series of experiments the indicated measurements were made as follows:

$\underline{p}_1$, $\underline{t}_1$, and the relative humidity of air at $\underline{t}_1$ were obtained as atmospheric measurements;

$\underline{v}$ was calculated from the measured geometry of the aging chambers;

$\underline{m}_1$ (100)/($\underline{s}$ + $\underline{m}_1$) and $\underline{s}$ were determined gravimetrically;

$\underline{t}_2$ was measured with a mercury thermometer; and

$\underline{p}_2$ was measured with a capillary-tube mercury manometer connected to an outlet in the cover of an aging chamber.

Results of these measurements are shown in Table XXV.

For an average value of p_2/p_1 of 1.72, Equation (1) reduces to

$$m_2 = \frac{973.3m_1 + 0.172s - 0.267v}{973} \qquad (2)$$

Values of m_2 for Experiments 2-5 are shown in Table XXIII.

In Figure 27 the fraction of the initial moisture retained at the terminal temperature, $m_2(100)/m_1$, is plotted as a function of the fraction of the chamber volume occupied by ovendry cellulose, $s(100)/\rho v$. This relationship is shown for cellulose containing 7.0, 5.5, and 4.0% moisture. The curve for 5.5% moisture is based on the data in Table XXV; curves for 7.0 and 4.0% moisture were calculated from Equation (2).

For 10 grams (O.D. basis) of cellulose containing 4.0% moisture at 23.3°C, the terminal moisture content would be 0.96(4.0%) or 3.84%; for 10 grams containing 5.5% moisture, the terminal moisture content would be 0.97(5.5%) or 5.34%; and for 10 grams containing 7.0% moisture the terminal moisture content would be 0.98(7.0%) or 6.86%.

At least 10 grams of linters were placed in each chamber for all trials.

TABLE XXV

DATA FOR MOISTURE CALCULATIONS

	Experiment Number				
	1	2	3	4	5
Initial Measurements:					
p_1, mm.	753.5	753.6	753.7	752.2	752.1
t_1, °C.	23.3	23.3	23.3	23.3	23.3
v, cc.	65.3	65.3	65.3	65.3	65.3
$m_1(100)/(m_1+s)$, %	--	5.5	5.5	5.5	5.5
(m_1+s), g.	--	3.175	6.350	12.450	21.510
m_1, g.	--	0.175	0.350	0.670	1.210
s, g.	--	3.000	6.000	11.780	20.300
Terminal Measurements:					
t_2, °C.	100	100	100	100	100
p_2(gauge), mm.	193.5	533.2	531.9	535.2	511.5
p_2(absolute), mm.	947.0	1286.8	1285.6	1287.4	1263.6
Calculated Results:					
p_2/p_1	1.257	1.708	1.706	1.712	1.670
p_2/p_1(corrected)[a]	1.263	1.723	1.722	1.728	1.697
$s(100)/\rho v$, %	--	2.97	5.93	11.6	20.1
m_2, g.	--	0.158	0.333	0.654	1.196
$m_2(100)/m_1$, %	--	90.0	95.1	97.6	98.8

[a] Corrected for manometer error

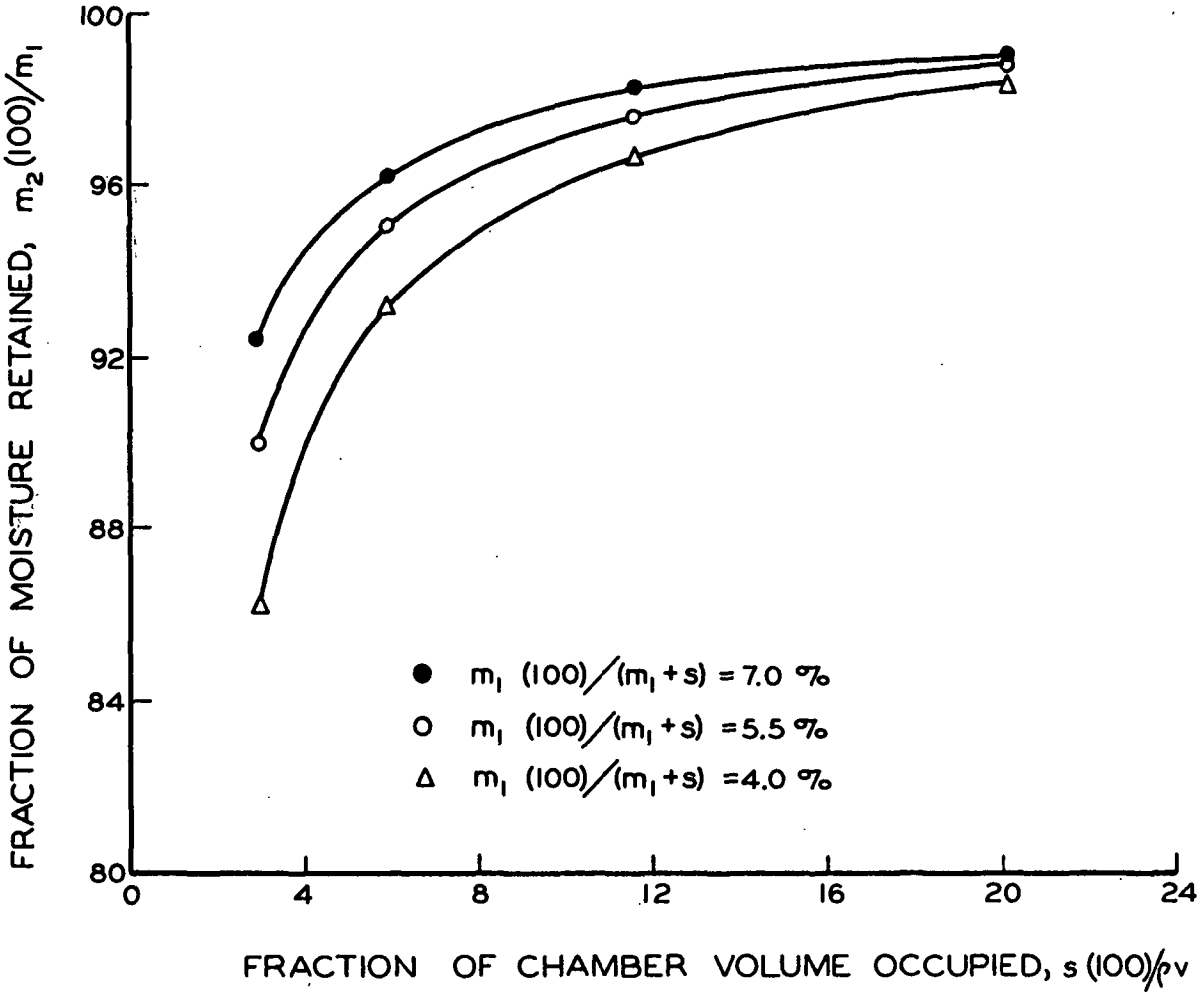

Figure 27. Fraction of Moisture Retained vs. Fraction of Chamber Volume Occupied

APPENDIX III

ANALYTICAL PROCEDURES

The following procedures were used for determining the metal content of cotton linters pulp.

WET OXIDATION (26)

Procedure

Weigh accurately a 1-g. specimen of pulp and transfer it to a 100-ml. Kjeldahl flask. Add 15 ml. of concentrated nitric acid and 2 ml. of concentrated sulfuric acid to the flask and heat over a low flame until the evolution of nitrous oxide fumes starts. Allow the reaction to continue without heating. As the reaction subsides add 2 ml. of concentrated perchloric acid and heat gently until the solution clears. Continue heating the clear solution until all nitric acid has been removed and strong fumes of perchloric acid are evolved. Allow the solution to cool and proceed with the determination of iron, manganese, or copper.

DETERMINATION OF IRON (26, 27)

Procedure

Transfer the oxidation solution to a 50-ml. volumetric flask. Rinse the digestion flask with 10 ml. of hot, 2N hydrochloric acid and several smaller portions of hot water, and add the washings to the volumetric flask before diluting to 50 ml. with deionized water. Pipet a 10-ml.

aliquot of the diluted oxidation solution into an Erlenmeyer flask, add 2 ml. of 10% hydroxylamine hydrochloride, 3 drops of methyl orange indicator, and titrate the mixture with 50% (7.5N) ammonium hydroxide. Note the amount of base required for neutralization. Pipet a second 10-ml. aliquot of the diluted oxidation solution into a 25-ml. volumetric flask and add 2 ml. of hydroxylamine hydrochloride and 2 ml. of 0.5% 1,10-phenanthroline. Mix the solution and slowly add the amount of ammonium hydroxide indicated by the previous titration. Dilute the solution to 25 ml. and measure its absorbance at 508 mmu in reference to a blank carried through the digestion and color formation steps.

Notes and Precautions

The sensitivity of this method, as determined from the slope of the calibration curve, was 7.68 absorbance units [one unit being equal to $(\log I_o/I) \times 10^3$] per microgram of iron. The average recovery of known amounts of iron was 98.8%.

The concentration of perchloric acid should not be permitted to exceed 0.4 ml. of concentrated acid per 25 ml. of the final solution. At higher concentrations a slightly soluble precipitate of 1,10-phenanthroline perchlorate was formed which caused low results when more than 10 micrograms of iron were present in the final solution.

The use of 2N hydrochloric acid in rinsing the digestion flask was necessary to assure complete transfer of iron from the digestion flask.

DETERMINATION OF MANGANESE (27)

Procedure

Transfer the oxidation solution to a 50-ml. volumetric flask. Rinse the digestion flask with several small portions of hot water and add the rinsings to the volumetric flask before diluting to 50 ml. with deionized water. Pipet 15 ml. of the diluted oxidation solution into a 25-ml. volumetric flask and add 1 ml. of a solution containing 75 g. of mercuric sulfate, 400 ml. of concentrated nitric acid, 200 ml. of 85% phosphoric acid, and 0.035 g. of silver nitrate per liter. Add 1 g. of ammonium persulfate and stir the mixture by swirling. Heat the flask and its contents on a steam bath or hot plate until color begins to develop (about 5 minutes). Continue heating the solution for a few minutes to assure complete oxidation, then allow it to cool and dilute to 25 ml. Measure the absorbance at 525 mmu in reference to a blank carried through both the digestion and color formation steps.

Notes and precautions

The sensitivity of this method was 1.72 absorbance units per microgram of manganese. The average recovery of known amounts of metal was 98.5%.

The total acidity of the solution immediately prior to color formation should be less than the equivalent of 4 ml. of concentrated sulfuric acid per 25 ml. of solution. Above this level the color was slow to develop and did not develop fully.

DETERMINATION OF COPPER (28)

Procedure

Dilute the oxidation solution to approximately 25 ml. in the digestion flask. Neutralize the solution with ammonium hydroxide, transfer it to a 100-ml. separatory funnel, and continue the color formation steps exactly as described by Borchardt and Butler (28).

Notes and Precautions

The sensitivity of this method was 34.5 absorbance units per microgram of copper. The average recovery of known amounts of copper was 99.5%.

APPENDIX IV

ANALYTICAL DATA FOR HMF

The results of exploratory experiments with known samples of HMF, hydroxymethylfuroic acid (HMFA), and glucose are summarized in the following paragraphs.

Extraction of dilute, aqueous solutions (100 micrograms solute per 100 ml. water) of HMF and HMFA with small volumes (20 ml.) of ethyl acetate, ethyl ether, or chloroform did not selectively remove the solute from the solution. The extractions were unsuccessful even when the aqueous phase was saturated with sodium chloride.

Evaporation of dilute, aqueous solutions (100 micrograms solute per 100 ml. water) of HMF and HMFA to a final volume of less than 0.5 ml. did not change the ultraviolet spectrum of either compound when the evaporations were carried out at 30°C. under reduced pressure.

Chromatographic solvent developers applied to HMF, HMFA, and glucose were:

ethyl acetate : acetic acid : water (9:2:2) (EAW) (47)

butanol : pyridine : water (10:3:3) (BPW) (48)

butanol : 15N ammonium hydroxide : water (50:2:28) (BAW) (49)

The R_f values of the known compounds with these developers are shown in Table XXVI.

Spots of the known compounds were identified on developed chromatograms

TABLE XXVI

ANALYTICAL DATA FOR HMF AND HMFA

	R_f Values[a] for the Following Compounds		
	HMF	HMFA	Glucose
Solvent Developers			
EAW	0.83	0.78	0.17
BPW	0.74	---	0.14
BAW	0.78	0.09	0.08

Color Reagent[b]	Color Reactions of the Following Compounds		
	HMF	HMFA	Glucose
pAHCl	+	-	+
DNPH	+	-	-
MM	+	+	+
Ultraviolet Lamp[c]	+	+	-

[a] The R_f value is the ratio of the distance the compound has traveled to the distance the solvent front has traveled.

[b] A discernible color reaction is signified by +; the absence of a color reaction is signified by -.

[c] Noticeable absorption of ultraviolet light is signified by +; the absence of absorption is signified by -.

with an ultraviolet lamp or one of the following color reagents:

p-anisidine hydrochloride (pAHCl) (50)

2,4-dinitrophenylhydrazine (DNPH) (51)

permanganate-periodate (PP) (52)

Results obtained for each color reagent and the ultraviolet lamp are summarized in Table XXVI.

The detection of HMF via infrared spectral analysis was not successful when alcoholic solutions of this compound were evaporated on potassium bromide pellets, and the per cent transmission of the pellets measured. Excessive "fogging" of the pellets appeared to be the cause of strong background absorption which obliterated any recognizable spectra.

HMF (purity $\geq$ 98%) (53) in the liquid phase, and solid HMFA (purity $\geq$ 99%) (53) pressed into potassium bromide pellets gave infrared transmission spectra characteristic for these compounds.

HMF in chloroform solution was identifiable via infrared analysis providing a sufficient amount of the material was present. HMF could not be identified in 0.25 ml. of a solution containing 1.0 mg. HMF per ml. of chloroform; it could, however, be identified in 0.25 ml. of a solution containing 15.4 mg. HMF per ml. of chloroform.

APPENDIX V

EXPERIMENTAL RESULTS

The conditions of aging and analytical results for all trials are given in the following tables.

TABLE XXVII

RESULTS OF TRIAL I

Aging Time, hours	Sample[b]	Absolute Reflectance[c], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.
0	Control[d]	91.6	314	1.21	—
	Ferric	82.0	298	5.89	2.37
	Ferrous	87.0	309	3.00	0.709
	Cupric	89.8	288	1.67	0.997
	Manganous	90.8	306	1.43	0.523
	Untreated[e]	90.4	282	1.45	—
2[a]	Control	90.6	320	1.58	
	Ferric	79.1	303	8.63	
	Ferrous	85.5	306	3.76	
	Cupric	89.0	289	1.96	
	Manganous	90.2	310	1.65	
	Untreated	89.6	282	1.72	
7[a]	Control	89.6	321	1.94	
	Ferric	78.2	306	9.39	
	Ferrous	84.7	310	4.28	
	Cupric	87.7	279	2.40	
	Manganous	89.5	301	1.85	
	Untreated	88.6	281	2.06	
18[a]	Control	88.3	347	2.68	
	Ferric	76.6	304	10.83	
	Ferrous	83.0	301	5.28	
	Cupric	83.8	284	4.45	
	Manganous	88.6	313	2.30	
	Untreated	87.3	274	2.55	
42[a]	Control	86.0	313	3.57	
	Ferric	71.1	306	18.8	
	Ferrous	78.9	306	8.63	
	Cupric	74.3	275	12.2	
	Manganous	87.6	309	2.71	
	Untreated	85.0	270	3.57	

[a] Aging was conducted at ~5% moisture and ~103°C.
[b] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.
[c] Measured at 460 mmu on the GERS.
[d] Acid-washed pulp.
[e] Untreated pulp as received from Buckeye Cellulose Corporation

TABLE XXVIII

VARIATION OF SPECIFIC ABSORPTION COEFFICIENT WITH WAVELENGTH (TRIAL I)

Aging Time, hours	Wavelength, mmu.	Absorption Coefficients, sq. cm./g. of Samples Containing the Following Sulfates:				
		Control	Ferric	Ferrous	Cupric	Manganous
0	400	1.72	16.0	7.26	2.29	1.90
	420	1.50	11.2	5.18	2.01	1.73
	440	1.35	8.00	3.61	1.81	1.53
	457	1.20	6.48	3.24	1.75	1.45
	460	1.21	5.89	3.00	1.67	1.43
	480	1.14	4.98	2.66	1.55	1.36
	500	1.05	4.04	2.25	1.50	1.30
	550	0.97	2.19	1.67	1.40	1.20
	600	0.92	1.49	1.37	1.38	1.10
	650	0.90	1.28	1.21	1.43	1.05
42[a]	400	5.92	34.7	15.5	20.4	4.15
	420	4.87	27.2	12.1	16.7	3.59
	440	4.31	21.9	10.1	14.5	3.08
	457	--	--	--	--	--
	460	3.57	18.8	8.63	12.2	2.71
	480	3.12	16.2	7.58	10.4	2.32
	500	2.75	13.8	6.51	9.17	2.16
	550	1.99	8.78	4.47	6.49	1.63
	600	1.51	5.57	3.07	4.53	1.35
	650	1.22	3.77	2.25	3.19	1.14

[a] Aging was conducted at ~5% moisture and ~103°C.

TABLE XXIX

RESULTS OF TRIAL II

Aging Time, hours	Sample[b]	Absolute Reflectance[c], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.
0	Control	90.0	270	1.37	--
	Control	89.9	278	1.58	--
	Cupric nitrate	89.7	279	1.65	--
	Cupric chloride	89.1	261	1.74	1.35
	Cupric sulfate	88.0	267	2.18	0.906
	Cupric ammonium sulfate	90.0	300	1.67	1.03
	Cupric acetate	89.9	280	1.68	0.980
42[a]	Control	86.5	271	2.86	
	Control	85.9	276	3.20	
	Cupric nitrate	81.5	273	5.73	
	Cupric chloride	80.5	266	6.29	
	Cupric sulfate	81.6	269	5.61	
	Cupric ammonium sulfate	82.4	303	5.69	
	Cupric acetate	82.3	277	5.28	

[a] Aging was conducted at ~4% moisture and ~100°C.

[b] The indicated salts were used; slurry concentration of metal was 1 p.p.m.

[c] Measured at 457 mmu on the GERS.

TABLE XXX

RESULTS OF TRIAL III

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.
0	Control	89.6	278	1.68	--
	Control	88.8	256	1.81	--
	Ferric	81.1	254	5.59	1.81
	Ferrous	85.6	278	3.25	0.835
	Cupric	87.4	259	2.35	1.18
	Manganous	89.6	291	1.76	1.26
0	Control	89.7	267	1.58	--
	Cupric	88.8	279	1.97	1.18
42[c]	Control	81.7	263	5.40	
	Control	79.6	254	6.62	
	Ferric	66.6	246	20.6	
	Ferrous	71.3	279	16.1	
	Cupric	69.4	259	17.5	
	Manganous	85.1	288	3.76	
42[d]	Control	88.2	269	2.12	
	Cupric	87.6	265	2.32	

[a] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Aging was conducted at ~5% moisture and ~103°C.

[d] Aging was conducted at 0% moisture and ~103°C.

TABLE XXXI

RESULTS OF TRIAL IVA

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.
0	Control	90.1	263	1.43	--
	Ferric	82.3	249	4.75	1.508
	Ferrous	87.6	263	2.31	0.756
	Cupric	89.4	269	1.69	1.405
	Manganous	89.9	281	1.59	1.135
	Sulfuric acid[c]	90.1	264	1.44	--
0	Control	90.0	264	1.47	--
	Ferric	82.4	277	5.21	1.550
	Ferrous	88.2	269	2.12	0.686
	Cupric	89.4	267	1.68	1.44
	Manganous	89.7	276	1.63	1.21
42[d]	Control	82.8	256	4.57	
	Ferric	73.1	254	12.6	
	Ferrous	76.7	261	9.25	
	Cupric	78.9	266	7.48	
	Manganous	87.0	276	2.68	
42[e]	Sulfuric acid[c]	84.3	256	3.75	
	Control	88.5	256	1.91	
	Ferric	79.6	267	6.98	
	Ferrous	85.4	269	3.36	
	Cupric	88.3	267	2.07	
	Manganous	88.9	270	1.87	

[a] Sulfates were used; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Pulp slurry was acidified to pH 4.0 prior to pad formation.

[d] Aging was conducted at 5.2% moisture and ~100°C.

[e] Aging was conducted at 0% moisture and ~100°C.

TABLE XXXII

RESULTS OF TRIAL IVB

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.
0	Control	89.1	274	1.83	--
	Cupric	87.9	268	2.23	1.318
	Manganous	88.9	272	1.88	0.727
42[c]	Control	81.0	276	6.15	
	Cupric	67.2	268	21.5	
	Manganous	82.4	261	4.90	
42[d]	Control	80.1	252	6.21	--
	Cupric	68.2	243	18.0	1.318
	Manganous	84.8	257	3.50	0.78
42[e]	Control	82.8	254	4.54	--
	Cupric	81.2	253	5.51	1.28
	Manganous	86.4	250	2.67	0.69

[a] Sulfate salts were used, slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Aging was conducted at 3.9% moisture and ~103°C.

[d] Aging was conducted at 6.8% moisture and ~103°C.

[e] Aging was conducted at 11.2% moisture and ~103°C.

TABLE XXXIII

RESULTS OF TRIAL V

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.	Intrinsic Viscosity, dl./g.
0	Control	89.9	262	1.50	--	13.9
	Ferric	81.8	268	5.42	1.442	13.8
	Ferrous	87.4	271	2.48	0.645	13.6
	Cupric	89.9	287	1.64	1.161	13.8
	Manganous	89.8	253	1.48	0.819	13.8
42[c]	Control	86.5	272	2.87		
	Ferric	77.9	272	8.55		
	Ferrous	82.7	272	4.93		
	Cupric	83.9	272	4.23		
	Manganous	85.4	272	3.39		
42[d]	Control	82.5	271	5.04		8.16
	Ferric	71.9	274	15.1		5.41
	Ferrous	77.1	279	9.48		5.10
	Cupric	77.9	291	9.17		6.40
	Manganous	84.4	269	3.93		8.62
42[e]	Control	81.9	272	5.45		
	Ferric	75.0	272	11.5		
	Ferrous	79.1	272	7.55		
	Cupric	79.3	272	7.34		
	Manganous	85.3	272	3.47		

TABLE XXXIII (continued)

RESULTS OF TRIAL V

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g	Metal Content, microgram-atoms/g.	Intrinsic Viscosity, dl./g.
42[f]	Control	83.0	272	4.77		
	Ferric	76.1	272	10.3		
	Ferrous	79.7	272	7.08		
	Cupric	82.6	272	5.02		
	Manganous	84.0	272	4.15		
42[g]	Control	83.0	272	4.77		
	Ferric	76.5	272	9.90		
	Ferrous	79.5	272	7.72		
	Cupric	81.8	272	5.51		
	Manganous	84.4	272	3.74		

[a] Sulfate salts were used, slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Aging was conducted at 0% moisture and 100°C.

[d] Aging was conducted at 4.1% moisture and 100°C.

[e] Aging was conducted at 7.1% moisture and 100°C.

[f] Aging was conducted at 10.1% moisture and 100°C.

[g] Aging was conducted at 11.3% moisture and 100°C.

TABLE XXXIV

RESULTS OF TRIAL VI

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.	Intrinsic Viscosity dl./g.
0	Control	90.2	270	1.45	--	13.7
	Ferric	83.0	275	4.79	1.541	13.6
	Ferrous	87.8	247	2.09	0.628	13.4
	Cupric	89.2	258	1.70	1.141	13.7
	Manganous	89.4	249	1.58	1.192	13.7
42[c]	Control	86.9	293	2.92		11.6
	Ferric	80.2	292	7.19		11.1
	Ferrous	83.7	270	4.30		10.6
	Cupric	86.4	297	3.20		11.5
	Manganous	85.4	276	3.44		12.1
42[d]	Control	79.5	273	7.20		4.56
	Ferric	55.7	273	48.0		1.45
	Ferrous	57.8	273	42.0		1.74
	Cupric	62.9	273	29.8		2.08
	Manganous	81.6	273	5.67		4.79
42[e]	Control	80.7	273	6.33		4.80
	Ferric	69.0	273	18.2		2.76
	Ferrous	73.1	273	13.5		3.45
	Cupric	73.1	273	13.6		2.65
	Manganous	85.0	273	3.61		5.65

TABLE XXXIV (continued)

RESULTS OF TRIAL VI

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.	Intrinsic Viscosity dl./g.
42[f]	Control	80.6	273	6.40		
	Ferric	73.2	273	13.4		
	Ferrous	75.6	273	10.7		
	Cupric	77.0	273	9.40		
	Manganous	83.9	273	4.23		
42[g]	Control	81.5	273	5.76		5.40
	Ferric	74.9	273	11.5		3.67
	Ferrous	78.7	273	7.88		3.86
	Cupric	81.2	273	5.94		3.14
	Manganous	83.5	273	4.44		6.30

[a] Sulfate salts added; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Aging was conducted at 0% moisture and 107°C.

[d] Aging was conducted at 4.2% moisture and 107°C.

[e] Aging was conducted at 6.9% moisture and 107°C.

[f] Aging was conducted at 9.4% moisture and 107°C.

[g] Aging was conducted at 11.4% moisture and 107°C.

TABLE XXXV

RESULTS OF TRIAL VII

Aging Time, hours	Sample	Absolute Reflectance[a], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.	Intrinsic Viscosity dl./g.
0[b]	Control	89.9	266	1.52	--	
	Ferric	82.6	267	4.93	1.528	
	Ferrous	87.2	239	2.24	1.145	
	Cupric	89.5	255	1.58	1.240	
	Manganous	89.6	254	1.54	0.940	
0[c]	Control	89.7	256	1.52	--	
	Ferric	62.7	256	28.4	6.58	
	Ferrous	86.2	256	2.85	1.111	
	Cupric	89.2	256	1.69	1.219	
	Manganous	89.2	256	1.69	0.927	
0[d]	Control	89.8	256	1.48	--	
	Ferric	71.5	256	14.6	5.29	
	Ferrous	--	256	--	--	
	Cupric	89.5	256	1.58	1.260	
	Manganous	89.9	256	1.47	1.094	
42[be]	Control	81.7	261	5.36		5.50
	Ferric	62.8	267	29.5		2.70
	Ferrous	63.9	252	25.7		2.70
	Cupric	70.5	250	15.5		2.87
	Manganous	84.4	250	3.63		6.11

TABLE XXXV (continued)

RESULTS OF TRIAL VII

Aging Time, hours	Sample	Absolute Reflectance[a], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.	Intrinsic Viscosity dl./g.
42[ce]	Control	84.2	256	3.82		6.09
	Ferric	56.8	256	42.1		4.08
	Ferrous	64.9	256	24.3		2.94
	Cupric	72.2	256	13.8		3.21
	Manganous	85.2	256	3.29		6.60
42[de]	Control	83.7	256	4.06		6.31
	Ferric	61.2	256	31.6		4.08
	Ferrous	—	256	—		—
	Cupric	71.8	256	14.2		2.93
	Manganous	85.8	256	3.01		6.71

[a] Measured at 457 mmu on the GERS.

[b] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.

[c] Chloride salts were used; slurry concentration of metal was 1 p.p.m.

[d] Acetate salts were used; slurry concentration of metal was 1 p.p.m.

[e] Aging was conducted at 4.3% moisture and 105°C.

TABLE XXXVI

RESULTS OF TRIAL VIII

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.
0[c]	Control	90.3	255	1.33	—
	Ferric	83.3	255	4.27	1.562
	Ferrous	87.7	255	2.20	0.689
	Cupric	88.7	255	1.84	0.821
	Manganous	89.6	255	1.56	0.906
0[d]	Control	90.4	250	1.28	—
	Ferric	83.0	257	4.50	1.377
	Ferrous	87.4	259	2.87	0.594
	Cupric	89.2	260	1.70	1.113
	Manganous	90.3	249	1.31	0.845
0[e]	Control	90.6	255	1.24	—
	Ferric	85.0	255	3.41	1.040
	Ferrous	88.5	255	1.93	0.453
	Cupric	90.0	255	1.42	1.272
	Manganous	90.4	255	1.30	1.021
42[cf]	Control	81.2	255	5.56	
	Ferric	58.6	255	37.2	
	Ferrous	60.8	255	32.2	
	Cupric	66.8	255	21.1	
	Manganous	83.6	255	4.13	
42[df]	Control	79.8	255	6.51	
	Ferric	57.9	255	39.2	
	Ferrous	60.1	255	33.8	
	Cupric	64.0	255	25.9	
	Manganous	82.5	255	4.76	
42[ef]	Control	80.8	255	5.84	
	Ferric	58.5	255	37.6	
	Ferrous	63.0	255	27.9	
	Cupric	64.3	255	25.3	
	Manganous	83.7	255	4.07	

[a] Sulfate salts were used.
[b] Measured at 457 mmu on the GERS.
[c] Slurry concentration of metal was 0.5 p.p.m.
[d] Slurry concentration of metal was 1.0 p.p.m.
[e] Slurry concentration of metal was 5.0 p.p.m.
[f] Aging was conducted at 4.2% moisture and 106°C.

TABLE XXXVII

RESULTS OF TRIAL IX

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.	Intrinsic Viscosity dl./g.
0	Control	91.1	279	1.23	—	
	Ferric	83.0	277	4.86	1.572	
	Ferrous	88.5	254	1.90	0.715	
	Cupric	90.4	265	1.34	0.986	
	Manganous	90.8	269	1.26	0.662	
42[c]	Control	83.6	269	4.33		5.98
	Ferric	61.5	269	32.4		2.29
	Ferrous	65.4	269	24.6		3.60
	Cupric	68.9	269	18.9		3.20
	Manganous	85.2	269	3.46		6.45
42[d]	Control	84.1	269	4.04		7.95
	Ferric	63.8	269	27.6		6.48
	Ferrous	68.2	269	20.0		6.75
	Cupric	70.9	269	16.1		8.40
	Manganous	86.1	269	3.02		8.40

[a] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Aging was conducted in 21% oxygen (air) at 4.2% moisture.

[d] Aging was conducted in <0.1% oxygen (nitrogen) at 4.2% moisture and 105°C.

TABLE XXXVIII

RESULTS OF TRIAL X

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Metal Content, microgram-atoms/g.
0[c]	Control	89.9	255	1.45	--
	Ferric	82.9	255	4.50	1.562
	Ferrous	87.3	255	2.36	0.689
	Cupric	88.8	255	1.80	0.821
	Manganous	89.7	255	1.51	0.906
0[d]	Control	90.1	257	1.40	
	Ferric	89.8	257	1.49	
	Ferrous	89.7	257	1.46	
	Cupric	90.2	257	1.37	
	Manganous	90.0	257	1.43	
42[ce]	Control	81.2	255	5.56	
	Ferric	59.9	255	34.2	
	Ferrous	62.0	255	29.7	
	Cupric	66.4	255	21.7	
	Manganous	83.4	255	4.21	
42[de]	Control	83.9	250	3.97	--
	Ferric	66.9	257	21.0	0.246
	Ferrous	68.2	257	19.0	0.112
	Cupric	71.7	259	14.4	0.064
	Manganous	85.4	262	3.21	0.000

[a] Sulfate salts were used; slurry concentration metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Unextracted samples.

[d] Samples extracted with dilute acid (0.1N HCl and 0.1N HF).

[e] Aging was conducted at 4.2% moisture and 106°C.

TABLE XXXIX

RESULTS OF TRIAL XI

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.
0	Control	90.5	267	1.33
	Ferric	82.6	253	4.62
	Manganous	90.6	267	1.30
	Magnesium	90.3	249	1.31
	Cadmium	90.8	251	1.17
	Lanthanum	90.6	266	1.30
42[c]	Control	80.6	259	6.05
	Ferric	56.7	259	42.8
	Manganous	84.3	259	3.79
	Magnesium	82.9	259	4.57
	Cadmium	82.8	259	4.63
	Lanthanum	82.9	259	4.57
42[d]	Control	82.2	259	5.00
	Ferric	63.5	259	27.2
	Manganous	85.6	259	3.14
	Magnesium	82.7	259	4.69
	Cadmium	82.3	259	4.93
	Lanthanum	83.1	259	4.45

[a] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Aging was conducted at 4.1% moisture and 106°C.

[d] Aging was conducted at 7.0% moisture and 106°C.

TABLE XL

RESULTS OF TRIAL XII

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.
0[c]	Control	90.6	256	1.24
	Ferric	82.0	255	5.07
	Manganous	90.6	250	1.23
0[d]	Control	90.6	250	1.28
	Ferric	80.1	263	6.72
	Manganous	90.6	258	1.27
42[ce]	Control	78.1	258	7.91
	Ferric	57.2	258	41.3
	Manganous	84.2	258	3.82
42[ce]	Control	79.4	258	6.87
	Ferric	59.6	258	35.3
	Manganous	83.3	258	4.31
42[cf]	Control	81.8	258	5.22
	Ferric	62.9	258	28.2
	Manganous	84.6	258	3.62
42[df]	Control	82.4	258	4.85
	Ferric	63.8	258	26.4
	Manganous	83.8	258	4.04

[a] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Unextracted pulp.

[d] Pulp extracted with acetone prior to pad formation.

[e] Aging was conducted at 3.7% moisture and 106°C.

[f] Aging was conducted at 6.0% moisture and 106°C.

TABLE XLI

RESULTS OF TRIAL XIII

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Intrinsic Viscosity dl./g.
0	Control	90.5	260	1.30	12.1
	Ferric	82.7	260	4.70	12.3
	Ferrous	88.0	260	2.13	12.3
	Cupric	89.4	260	1.63	12.2
	Manganous	90.6	260	1.27	12.4
2[c]	Control	88.6	260	1.90	11.6
	Ferric	74.7	260	11.1	11.5
	Ferrous	85.8	260	3.06	11.5
	Cupric	87.4	260	2.36	11.0
	Manganous	88.9	260	1.80	11.7
6[c]	Control	87.6	260	2.28	10.8
	Ferric	73.9	260	12.0	10.1
	Ferrous	84.2	260	3.86	10.2
	Cupric	85.8	260	3.06	9.00
	Manganous	88.0	260	2.13	11.1
18[c]	Control	85.8	260	3.06	8.18
	Ferric	70.7	260	15.8	7.04
	Ferrous	79.8	260	6.65	6.88
	Cupric	81.6	260	5.40	5.59
	Manganous	87.1	260	2.48	8.59
42[c]	Control	82.6	260	4.76	5.53
	Ferric	61.4	260	31.6	1.98
	Ferrous	65.6	260	23.5	2.73
	Cupric	69.3	260	17.7	3.21
	Manganous	84.8	260	3.54	5.82
66[c]	Control	79.1	260	7.20	4.29
	Ferric	50.3	260	64.0	1.22
	Ferrous	54.4	260	49.8	1.77
	Cupric	59.4	260	36.2	2.08
	Manganous	81.5	260	5.46	4.61

[a] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.
[b] Measured at 457 mmu on the GERS.
[c] Aging was conducted at 4.3% moisture and 105°C.

TABLE XLII

RESULTS OF TRIAL XIVA

Aging Time, hours	Sample[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.
0[c]	Control	90.3	255	1.33
	Ferric	82.5	263	4.89
	Ferrous	88.9	270	1.88
	Cupric	89.9	280	1.59
	Manganous	90.5	241	1.20
2[ce]	Control	89.0	259	1.75
	Ferric	76.0	259	9.81
	Ferrous	85.8	259	3.04
	Cupric	88.0	259	2.12
	Manganous	89.2	259	1.69
2[de]	Control	89.3	257	1.66
	Ferric	88.5	253	1.89
	Ferrous	89.0	267	1.82
	Cupric	88.6	254	1.86
	Manganous	89.0	254	1.72

[a] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Unextracted samples.

[d] Samples extracted with dilute acid (0.1N HCl and 0.1N HF).

[e] Aging was conducted at 4.0% moisture and 105°C.

TABLE XLIII

RESULTS OF TRIAL XIVB

Aging Time, hours	Samples[a]	Absolute Reflectance[b], %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.	Intrinsic Viscosity, dl./g.
0	Control	90.6	259	1.26	--
	Ferric sulfate	83.0	259	4.51	--
	Ferric chloride	63.7	259	26.8	--
	Ferric acetate	69.3	259	17.6	--
0	Control	90.6	259	1.26	--
	Sulfuric acid[c]	90.5	259	1.30	--
	Ferric sulfate	82.8	259	4.63	--
	Aluminum sulfate	91.0	259	1.16	--
42[d]	Control	84.0	259	3.95	--
	Ferric sulfate	63.5	259	27.2	--
	Ferric chloride	56.7	259	42.8	--
	Ferric acetate	61.6	259	31.0	--
42[d]	Control	84.0	259	3.95	5.44
	Sulfuric acid[c]	75.1	259	10.7[e]	1.29
	Ferric sulfate	62.0	259	30.2	1.93
	Aluminum sulfate	82.4	259	4.87	5.44

[a] The indicated salts were used; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] 2.3 Micromoles of acid were added to each disk.

[d] Aging was conducted at 4.0% moisture and 105°C.

[e] The edges of these disks were black.

TABLE XLIV

RESULTS OF TRIAL XIVC

Aging Time, hours	Samples[a]	Absolute Reflectance,[b] %	Specific Scattering Coefficient, sq. cm./g.	Specific Absorption Coefficient, sq. cm./g.
0	Control	89.6	259	1.56
	Cadmium	90.2	259	1.38
	Lanthanum	89.6	259	1.56
	Magnesium	89.7	259	1.53
42[c]	Control	81.0	259	5.80
	Cadmium	82.3	259	4.92
	Lanthanum	81.8	259	5.23
	Magnesium	81.9	259	5.18

[a] Sulfate salts were used; slurry concentration of metal was 1 p.p.m.

[b] Measured at 457 mmu on the GERS.

[c] Aging was conducted at 4.0% moisture and 105°C.

APPENDIX VI

KINETIC CALCULATIONS

For $$\frac{dy}{dt} = r_1 - r_2 y$$

$$\int_0^y \frac{dy}{(r_1 - r_2 y)} = \int_0^t dt$$

$$-\frac{1}{r_2} \ln (r_1 - r_2 y) \Big]_0^y = t \Big]_0^t$$

$$-\frac{1}{r_2} \ln (r_1 - r_2 y) + \frac{1}{r_2} \ln r_1 = t$$

$$\ln \left(\frac{r_1}{r_1 - r_2 y} \right) = r_2 t$$

$$\frac{r_1}{r_1 - r_2 y} = e^{r_2 t}$$

$$r_1 = r_1 e^{r_2 t} - r_2 y e^{r_2 t}$$

$$y = \frac{r_1 e^{r_2 t} - r_1}{r_2 e^{r_2 t}}$$

Now for $$\frac{dz}{dt} = r_2 y$$

$$\int_0^z dz = r_2 \int_0^t y\,dt = r_2 \int_0^t \left(\frac{r_1 e^{r_2 t} - r_1}{r_2 e^{r_2 t}} \right) dt$$

$$\int_0^z dz = \int_0^t r_1\,dt - \int_0^t r_1 e^{-r_2 t}\,dt$$

$$\left[\underline{z}\right]_0^{\underline{z}} = \underline{r}_1\left[\underline{t}\right]_0^{\underline{t}} - \underline{r}_1\left(\frac{-1}{\underline{r}_2}e^{-\underline{r}_2\underline{t}}\right)\Bigg]_0^{\underline{t}}$$

$$\underline{z} = \underline{r}_1\underline{t} + \frac{\underline{r}_1}{\underline{r}_2}e^{-\underline{r}_2\underline{t}} - \frac{\underline{r}_1}{\underline{r}_2}$$

$$\underline{z} = \underline{r}_1\left(\underline{t} + e^{-\underline{r}_2\underline{t}}/\underline{r}_2 - 1/\underline{r}_2\right)$$